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PHOSPHORUS CONTENT OF CITRUS AND FACTORS AFFECTING IT

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During an investigation of the phosphate nutrition of citrus, it was found that very few data were available regarding the phosphorus content of various portions of citrus trees. In order to supply this need and to study possible interrelations with other constituents, this factor was investigated; portions of the data obtained are here briefly described.

Total phosphorus in the dry matter was determined by the ashing method employed by Howk and DeTurk (11), followed by the molybdenum blue colorimetric method essentially as used by Truog and Meyer (14). The various phosphorus fractions in the dry matter were determined by the method of DeTurk, Holbert, and Howk (2).

PHOSPHORUS IN CITRUS FRUITS

Lemon fruits from Santa Barbara and Riverside. During the spring of 1929, samples of Eureka lemons of various sizes were collected both at Santa Barbara and in field 3 at the Citrus Experiment Station; samples of Lisbon lemons were collected at Santa Barbara only. Data for the average fresh and dry weights per fruit (grams), the size class, the color, the percentage of phosphorus in the dry matter, and the average phosphorus content per fruit (grams) were obtained.

The flowers were found to contain the highest percentage of phosphorus of any stage in the fruiting process. The data obtained indicate the need of caution when dealing with tree-ripe fruits. If we do not consider these fruits, the percentage of phosphorus in the dry matter of lemons shows a decrease with increasing maturity of the fruit. In some cases the percentage of phosphorus in tree-ripe lemons shows an increase, and in some cases a decrease as compared with silver-stage fruit. Tree-ripe fruits from the different locations show approximately the same percentages of phosphorus in the dry matter. After maturity is reached, the fruits while attached to the tree apparently undergo changes, as regards phosphorus, that differ from those of the green stages. In addition, marked changes occur in the dry matter, the basis on which calculations are frequently made.

The average phosphorus content per fruit (grams) at various stages of growth is plotted in figure 1 against the average dry weight per fruit (grams). The graphs show that the content of phosphorus (grams) per average fruit becomes

greater with increasing maturity of the fruit and may be considered as a possible rough measure of fruit maturity. Gray (6) considers the effect of phosphates to be one of hastening the maturity of navel oranges. In the case of lemons from Riverside it is seen that after the fruits become a certain size, or have a given dry weight, the phosphorus content (grams) exceeds that of fruits from Santa Barbara. Since green fruits of a given size are most desirable in lemons, if the phosphorus content is a criterion of the degree of maturity,

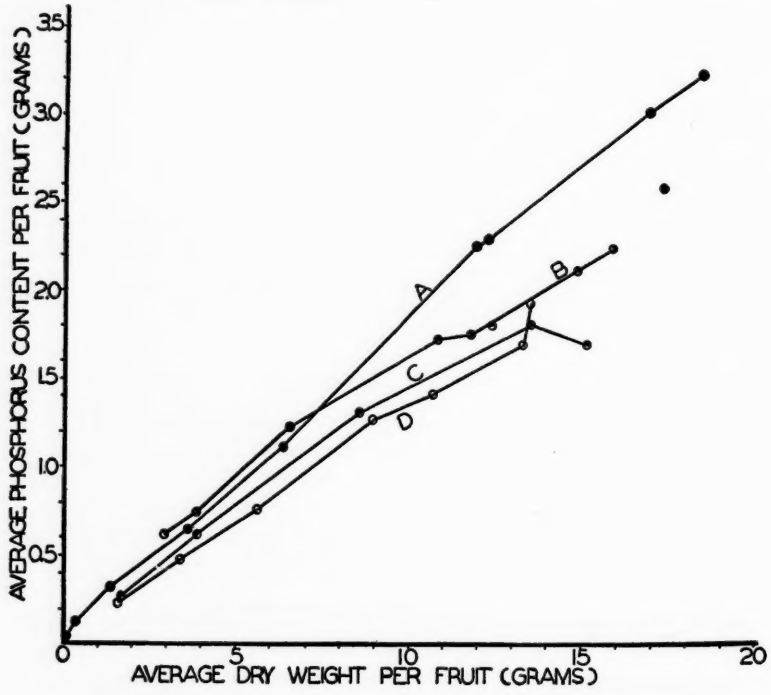

FIG. 1. RELATION OF AVERAGE DRY WEIGHT PER FRUIT (GRAMS) TO THE AVERAGE PHOSPHORUS CONTENT PER FRUIT (GRAMS) IN LEMON FRUITS

A, Eureka lemons collected April 16, 1929, at Riverside; *B*, Eureka lemons collected April 16, 1929, at Santa Barbara; *C*, Eureka lemons collected May 15, 1929, at Santa Barbara; and *D*, Lisbon lemons collected April 16, 1929, at Santa Barbara.

then Riverside fruits possibly do not remain in the green stage so long as do fruits at Santa Barbara. The increased phosphorus content of lemons at Riverside is of interest because of the prevalence of mottle-leaf in that citrus-growing area, and, as will be shown later, mottled leaves are uniformly richer in phosphorus than are healthy leaves grown under the same conditions.

A further point of interest in figure 1 is that Lisbon lemons of a given degree of size or dry weight contain less phosphorus than Eureka lemons grown under

the same environmental conditions. The growth of Lisbon lemon trees is usually more vigorous than that of Eureka lemon, and consequently a greater share of the phosphorus supply would be required for the increased vegetative growth, leaving less phosphorus available for the fruit. Furthermore, the active vegetative condition possibly would make a greater supply of organic materials available to the fruit and hence further dilute the phosphorus present.

TABLE 1

Phosphorus (P) content in fruits from trees in plots of Rubidoux fertilizer trials

(Per cent in dry matter)

PLOT	SOIL TREATMENT	VALENCIA ORANGES (PICKED MAY 15, 1929)		WASHINGTON NAVEL ORANGES (PICKED DEC. 19, 1929)		LEMONS (PICKED FEB. 25, 1930)	
		Peel	Pulp with seed	Peel	Pulp	Peel	Pulp with seed
A	Complete: Nitrate of soda, blood, bone, and sulfate of potash	.0725	.1938	.0688	.1531	.1900	.2600
B	No fertilizer	.0750	.1850	.0750	.2188	.1391	.2575
C	Dried blood	.0725	.1656	.0700	.1750	.1225	.2100
D	Sulfate of potash	.0738	.1900	.0988	.2500	.1425	.2350
E	Steamed bone	.0688	.1800	.0838	.2125	.....	.2438
F	Stable manure	.0600	.1656	.0713	.1750	.1325	.2375
G	Nitrate of soda, blood, and bone	.0600	.1725	.0650	.1719	.1338	.2150
H	Nitrate of soda	.1125	.2750	.0713	.1850	.2175	.2700
I	Muriate of potash	.0756	.1950	.0838	.2000	.1400	.2600
J	Superphosphate	.0775	.2100	.0813	.2150	.1450	.2563
K	Steamed bone and sulfate of potash	.0713	.1700	.0900	.2063	.1400	.2375
L	Nitrate of soda, blood, and sulfate of potash	.0688	.1863	.0663	.2000	.1375	.2188
M	No fertilizer	.0669	.1950	.0825	.2000	.1325	.2500
N	Superphosphate and blood to equal nitrogen in bone plots	.0700	.1900	.0650	.2000	.1125	.2500
O	Stable manure and rock phosphate	.0650	.1688	.0750	.1750	.1200	.2313
P	Steamed bone	.0600	.1563	.0900	.2000	.1375	.2400
Q	Complete: Nitrate of soda, blood, superphosphate, and sulfate of potash	.0638	.1719	.0713	.1800	.1075	.2200
R	Sulfate of potash	.0700	.1850	.0788	.2000	.1275	.2500
S	Dried blood	.0588	.1500	.0750	.1800	.0963	.2125
T	Unfertilized	.0750	.2000	.0838	.2200	.1225	.2250
U	Manure, rock phosphate, and covercrop	.....	.....	.....	.2000	.....	.....
V	Manure, rock phosphate, and covercrop	.....	.....	.0750	.1875	.....	.....

The phosphorus content of lemon fruits is a linear function of their dry weight; therefore the absolute amount of phosphorus (grams) continually increases in a fruit until it becomes mature. This phosphorus supply may be made available even to trees grown in soil solutions which contain relatively low phosphate concentrations. Burd and Martin (1) have demonstrated with water as the displacing agent that repeated displacement of the same mass of

soil with equal volumes of water results in a decreasing total concentration of electrolytes but usually in an increase in the phosphate concentration. The concentration of available phosphate therefore depends on the concentration of the other solutes and the reaction of their solutions.

Phosphorus in peel and pulp of fruits from trees in plots of the Rubidoux fertilizer trials. In 1929 samples of Valencia and Washington navel oranges, and in 1930 of lemon fruits, were collected from trees in the plots of the Rubidoux fertilizer trials. The peel was kept separate from the pulp. The data for the percentage of phosphorus (P) in the dry matter in relation to the soil fertilization are given in table 1. It is seen that the dry matter of the peel of lemons in general contains a higher percentage of phosphorus (average 0.1366) than that of the peel of oranges (average for Valencia orange peel 0.0709 and for Washington navel orange peel 0.0772). If averages are considered, the percentage of phosphorus in the dry matter of Valencia orange pulp was 0.1853, in Washington navel orange pulp 0.1958, and in lemon pulp 0.2390. The same general relation found in the peel holds also in the pulp. The peel or pulp of Valencia and Washington navel oranges showed no differences in percentages that could be related to the variety. Valencia orange and lemon peel or pulp from fruits of plot H that received nitrate of soda as its fertilizer treatment, contained markedly higher percentages of phosphorus than the peel or pulp of fruit from the Washington navel orange trees of that plot or of the other plots. The juice of Washington navel oranges from plot H was found to contain more inorganic phosphorus than that from the same variety of fruit from the other Rubidoux plots (8).

Examination of the trees of plot H in the rows in the field (15, p. 480) makes clear the following facts: From the irrigation standpipe at the head of the tree rows in plot H the trees are planted down the row in the order Washington navel orange, Valencia orange, Eureka lemon, and Lisbon lemon. The soil near the leaking standpipes received surface seepage water which did not extend beyond the Washington navel orange trees. Hence the navel orange trees were grown in a somewhat better-leached soil from which salts could move; the remaining trees in the rows were subject to the injurious physical and chemical effects of sodium salts on the soil. The effect of this more or less slow but continual leaching of the soil in which the navel orange trees were grown so improved the general appearance of these trees that it was almost impossible in 1929 to find a sufficient number of mottled leaves to serve as a sample. The beneficial effect of the slow leaching of the soil treated with sodium nitrate is evident from the fact that when Valencia orange trees were grown in soil in large tanks 8 feet in diameter by 4 feet deep and the soil was not permitted to become dry and was well drained, none of the injurious symptoms found in the Valencia orange or lemon trees of plot H were seen.

From a study of the pH of soil samples taken from plot H it is clear that if the first few drops of soil solution obtained by water displacement is tested, alkalinity to phenolphthalein may be obtained. Many of the plots of the Rubidoux trials far exceed the alkalinity of pH 7.6 without showing symptoms

of phosphate deficiency in the trees. Teakle (13) suggests that the hydroxyl ion alone probably causes the formation of a basic phosphate liberating some phosphate ions.

Phosphorus in Valencia oranges grown in solution cultures and in the field. Many of the leafy-twig cuttings produced fruit, as can be seen in figure 1

TABLE 2

Phosphorus in Valencia oranges grown on trees in phosphate-deficient or complete culture solutions, or on trees in the field at the Citrus Experiment Station

VARIETY	GROWN IN	CONDITION AND PORTION OF FRUIT USED	PHOSPHORUS IN DRY MATTER
			per cent
Valencia orange fruits from cutting grown on Lisbon lemon cutting as stock	Water culture (PO_4 absent)	1 fruit 3.5 cm. x 4 cm. long; 1 fruit 4 cm. x 4.5 cm. long; green; whole fruit	.0627
Valencia orange fruits from cutting	Water culture (PO_4 absent)	1 fruit 4.5 cm. x 4.5 cm. long; 1 fruit 4.5 cm. x 4 cm. long; green; whole fruit	.0560
Valencia orange fruit from cutting grown on Eureka lemon cutting as stock	Water culture (PO_4 absent)	1 fruit; full, ripe color; whole fruit	.0519
Valencia orange fruit from cutting grown on Lisbon lemon cutting as stock	Water culture (PO_4 absent)	1 fruit; full, ripe color; whole fruit	.0575
Valencia orange fruits from cutting grown on Rough lemon cutting as stock	Complete culture solution	1 fruit 6 cm. x 7 cm. long; 1 fruit 7 cm. x 7.5 cm. long; green; whole fruit	.2125
Valencia oranges from trees in plant pathology plot	Soil in field	5 fruits, mature; June 15, 1934; pulp (whole with seed); no peel	.2313
Valencia orange fruits plot I, R1, T29, Box Springs	Soil in field	22 young fruits, July 17, 1929; no buttons; fruits variable in size; whole fruit	.1959
Valencia orange fruits plot E, R1, T10, Box Springs	Soil in field	26 young fruits, July 17, 1929; no buttons; fruits variable in wise; whole fruit	.1959
Valencia orange fruits plot I, R45, T41, Box Springs	Soil in field	20 fruits, July 17, 1929; no buttons; fruits just shedding the style after the loss of petals; 2 to 2.5 cm. dia. x 2.5 to 3 cm. long; whole fruit	.1959
Valencia orange fruits block K, R45 (C)	Soil in field	35 young fruits, July 17, 1929; no buttons; fruits 2.5 cm. dia. x 3 cm. long; whole fruit	.2084

of plate 1. Some of these fruits were produced on cuttings grown in phosphate-deficient culture solutions, whereas others were produced by cuttings in complete culture solutions (control). For purposes of comparison, fruits of different ages were obtained from the field plots at the Citrus Experiment Station.

The results of the analyses for phosphorus are given in table 2. In the ab-

sence of phosphorus in the culture solution the percentage of phosphorus in the dry matter of Valencia oranges was between 0.0519 and 0.0575 for ripe fruit and slightly higher for smaller green fruit. When Valencia orange fruits were grown on cuttings in a complete culture solution containing 105 p.p.m. phosphate, the percentage of phosphorus in the dry matter was 0.2125, or approximately four times as high. Since many oranges grown on cuttings in culture solutions showed most severe granulation, the need for water is probably not a factor in the production of this physiological disease of Citrus fruits.

TABLE 3

Phosphorus in the peel of citrus fruits grown on trees in phosphate-deficient or complete solution cultures or on trees in the field at the Citrus Experiment Station

VARIETY	GROWN IN	CONDITION AND PORTION OF FRUIT USED	PHOSPHORUS (P) AS A PER CENT OF DRY MATTER IN			
			Stem half of peel		Tip half of peel	
			Inner portion	Outer portion	Inner portion	Outer portion
Valencia orange fruit from cutting grown on Eureka lemon cutting as stock	Water culture (PO_4 absent)	1 fruit; full ripe color; June 13, 1934	.0298	.0338	.0351	.0482
Valencia orange fruit from cutting grown on Lisbon lemon cutting as stock	Water culture (PO_4 absent)	1 fruit; full ripe color; June 13, 1934	.0191	.0233	.0223	.0283
Washington navel orange fruit from cutting grown on Rough lemon cutting as stock	Water culture (complete nutrient)	1 fruit, 6 cm. x 7 cm. long; 1 fruit, 7 cm. x 7.5 cm. long; green; June 13, 1934	.0483	.0659	.0529	.0889
Valencia orange fruit from trees in plant pathology plot	Soil in field	5 mature fruits; June 15, 1934	.0838	.1250	.1025	.1775

The dry matter of the whole pulp of Valencia oranges from the field contained 0.2313 per cent phosphorus. Four lots of the young oranges obtained in the field showed approximately 0.2 per cent of phosphorus in the dry matter of the whole fruit.

Phosphorus in peel of oranges grown on trees in phosphate-deficient or complete culture solutions, or on trees in the field. The stem and tip halves of the peel were divided into inner and outer portions. The latter included the oil glands. The data in table 3 show the distribution of phosphorus in the peel. The outer portion of the dry matter contains a greater percentage of phosphorus than the inner portion in both the stem and tip halves. The values for the tip halves exceed those for the stem halves. Phosphorus-free culture solutions permitted the growth of fruit but produced a marked reduction in the

percentage of phosphorus in the dry matter of the peel as compared with nearly ripe fruit grown on cuttings in complete culture solution.

The phosphorus content of citrus peel is of importance because of its possible relation to the oil of the peel. A sample of 10 cc. of commercial cold-pressed oil of orange showed 43 p.p.m. of phosphorus (if the specific gravity of the oil is assumed to be 1). The oil in the glands in the peel of Citrus fruits offers certain advantages to the fruit, such as protection; but at the same time there are disadvantages, such as occur when oil glands are injured and the oil itself injures otherwise healthy tissue. We invariably consider injury occurring to oil glands as being induced by mechanical abrasions, high temperatures, humidity, or water as shown by Fawcett, Klotz, and Haas (4). The possibility also exists that oils such as occur in Citrus peel contain certain fairly wide ranges of concentration of constituents such as phosphorus; when such concentrations are deficient or excessive, an instability may occur. Such oil composition possibly is a factor in the keeping quality of fruit under various

TABLE 4

Phosphorus fractions of Valencia orange peel

	PORTION USED	PHOSPHORUS AS PER CENT OF DRY MATTER		
		Inorganic	Organic	Phospholipid
5 Valencia oranges, pathology plot, June 15, 1934	Stem half, inner portion	.080	.017	.014
	Stem half, outer portion	.093	.025	.015
	Tip half, inner portion	.085	.027	.016
	Tip half, outer portion	.128	.037	.016
7 Valencia oranges, Rancho Santa Fe, San Diego County, October 2, 1933	Stem half	.068	.015	.011
	Tip half	.076	.020	.012

packing-house and transportation conditions. The writer soon became aware of the fact that losses of oil, for example in drying samples of avocado fruits, occasion considerable losses in the phosphorus content. More information is needed regarding oil stability and its corresponding composition when fruits are grown under certain nutrient deficiencies. In addition to total phosphorus, data regarding the phosphorus fractions of Valencia orange peel are necessary for a more complete understanding of the phosphorus nutrition.

Phosphorus fractions in Valencia orange peel. The percentages of inorganic, organic, and phospholipid phosphorus in the dry matter of the peel of Valencia oranges obtained at Riverside and at Rancho Santa Fe were determined. The differences in inorganic and organic phosphorus occur in the same direction as that described for total phosphorus in table 3. The percentages of phospholipid phosphorus show the smallest differences, but these are in the same direction as those of the organic and inorganic phosphorus. The percentages of organic phosphorus slightly exceed those of phospholipid phosphorus and are considerably less than those of inorganic phosphorus (table 4).

Haas and Klotz (10) found a greater amount of oil in the peel of the stylar (tip) end of Valencia oranges than in that of the calyx (stem) end. As has just been discussed in connection with the possible relationship of phosphorus

TABLE 5

Phosphorus content of healthy citrus leaves

VARIETY		DATE OF COLLECTION	LOCATION	PHOSPHORUS (P) IN DRY MATTER
Scion	Rootstock			
				per cent
Eureka lemon	Trifoliate orange	Dec. 16, 1925	Rubidoux plots	.1150
Eureka lemon	Pomelo	.....	Rubidoux plots	.1050
Eureka lemon	Sweet orange	June 22, 1927	Rubidoux, plot B	.1656
Eureka lemon	.....	.....	Santa Barbara	.1425
Eureka lemon	.....	Aug. 23, 1927	Irvine	.0900
Eureka lemon	Pomelo	Jan. 25, 1928	Rubidoux, plot U	.1200
Eureka lemon	Sweet orange	Sept. 13, 1926	Rubidoux, plot T	.1625
Eureka lemon	Sour orange	Feb. 16, 1928	Rubidoux, plot U	.1100
Eureka lemon	Sweet orange	Feb. 16, 1928	Rubidoux, plot U	.1300
Lisbon lemon	Sweet orange	Oct. 14, 1927	Rubidoux, plot E	.1400
Lisbon lemon	Sweet orange	Aug. 17, 1927	Rubidoux, plot M	.1875
Lisbon lemon	Sweet orange	Aug. 17, 1927	Rubidoux, plot L	.0950
Lemon	Sweet orange	Aug. 17, 1927	Rubidoux, plot Q	.0950
Lemon	.....	.....	Santa Paula	.1374
Lemon	Sweet orange	.....	Rubidoux, plot N	.1375
Washington navel orange	Trifoliate orange	Dec. 21, 1925	Rubidoux plots	.1244
Washington navel orange	Sweet orange	Dec. 16, 1925	Rubidoux plots	.1250
Washington navel orange	.....	July 19, 1928	Porterville	.1125
Washington navel orange	.....	Nov. 12, 1930	Alta Loma	.1250
Valencia orange	Trifoliate orange	Dec. 16, 1925	Rubidoux plots	.1175
Valencia orange	Sweet orange	Dec. 31, 1925	Rubidoux plots	.1088
Valencia orange	Sour orange	Dec. 16, 1925	Rubidoux plots	.1238
Valencia orange	Pomelo	Dec. 21, 1925	Rubidoux plots	.1250
Valencia orange	.....	Oct. 28, 1930	Whittier	.0838
Valencia orange	.....	May 23, 1929	Escondido	.0750
Valencia orange	.....	April 14, 1929	Orange	.0838
Valencia orange	.....	May 22, 1929	Rancho Santa Fe	.0925
Valencia orange	.....	April 22, 1929	Tulare	.0913
Florida sour orange	Seedling	Aug. 5, 1927	Rubidoux plots	.1188
Mediterranean sweet orange	Seedling	.....	Rubidoux, plot U	.1350

to oil, the phosphorus fractions follow the same direction as that found by these investigators for the oil of Valencia orange peel.

Healthy citrus leaves from trees grown in soil. Although phosphorus is one of the chief constituents of a complete fertilizer, very few data are available

in regard to the phosphorus content of citrus leaves. Kelley and Cummins (12) presented some of the first reliable data in 1920 as analyses of controls in a study of mottled leaves, but their data are unfortunately most limited. More complete data are necessary, therefore, for a clearer conception of the range of the phosphorus content of leaves in the field and for later comparison with data obtained in artificial cultures under known conditions of phosphorus deficiency. Accordingly, the percentage of total phosphorus was determined in the dry matter of healthy citrus leaves of different varieties grown under widely different soil conditions and collected during a considerable period. The results are given in table 5. The dry matter of Eureka lemon leaves contained from 0.0900 to 0.1656 per cent of phosphorus, the lowest value being for leaves from trees at Irvine and the highest for leaves from trees on a check (no fertilizer) plot at the Rubidoux fertilizer trials. The results for phosphorus in Lisbon lemon leaves, which are confined to those for leaves of the trees on the Rubidoux plots, vary from 0.0950 to 0.1875 per cent in the dry matter. The phosphorus in Washington navel orange leaves varied from 0.1125 to 0.1250 per cent; that in Valencia orange varied from 0.0750 at Escondido to 0.1250 per cent at the Rubidoux plots. The values for Valencia orange leaves are uniformly higher for trees of the Rubidoux plots than for five other scattered locations. As we shall see in table 7, one may not conclude from the results shown in table 5 that the trees the leaves of which show the lowest values are deficient in phosphorus. Other factors must be taken into consideration.

Effect of mottling and of soil fertilization. At various times during 1930, healthy leaves and, whenever available, also mottled leaves were collected from the several groups of trees grown in the pathology plots at Riverside. Each of the various groups of trees represented a different combination of scion and stock. These trees were grown in soil that was given a uniform fertilizer treatment of a type used in profitable commercial practice. The percentage of phosphorus was determined in the dry matter of the leaf samples; and the results are shown in table 6.

In every case in which mottled leaves were available, they contained markedly higher percentages of phosphorus than did healthy leaves. Leaf samples collected at Hemet showed similar results. These findings confirm those of Kelley and Cummins (12). It is essential, therefore, in obtaining leaves for chemical analysis to avoid mottled leaves and to collect only healthy ones. The results in table 6 show no relation between the scion and stock and the percentage of total phosphorus.

The results thus far described regarding the phosphorus content of citrus leaves have dealt, first, with leaves from widely scattered locations in which the soil, fertilization, irrigation, climatic conditions, and other practices varied considerably; and secondly, with leaves from a uniformly treated grove in which the several varieties of trees were grown approximately under the same conditions. Consideration was next given a study of the relation of a single

practice such as fertilization to the phosphorus content of citrus leaves, with the full realization, however, that the fertilization of soil is not a simple process and that it may result in both physical and chemical changes in the soil with corresponding changes in other relations.

These leaf samples, which consisted of healthy and mottled leaves, were obtained in 1933 from Valencia orange trees grown on the various plots of the Rubidoux fertilizer trials. The healthy and the mottled leaves were collected from side by side positions, or close to one another on the same trees. All of the trees in plots A to T are budded on sweet orange rootstocks, and the trees chosen in plot V (rootstock plot) were also those on sweet orange.

TABLE 6

Phosphorus content of gram aliquots of samples of citrus leaves obtained from mottled trees

SCION	ORANGE STOCK	LEAF SAMPLES COLLECTED	LOCATION	PHOSPHORUS IN DRY MATTER OF LEAVES	
				Healthy	Mottled
				per cent	*per cent*
Valencia	.....	Jan. 14, 1931	Hemet	.1075	.1400
Valencia orange	Sweet	Oct. 3, 1930	Pathology plots, Riverside	.1425	.2200
Navel orange	Sweet	Oct. 3, 1930		.2000	.....
Navel orange	Sweet	Dec. 11, 1930		.1925	.2600
Navel orange	Sour	Oct. 3, 1930		.1600	.2375
Navel orange	Sour	Dec. 11, 1930		.2000	.....
Marsh grapefruit	Sweet	Oct. 3, 1930		.1525	.....
Marsh grapefruit	Sweet	Dec. 11, 1930		.1000	.1650
Marsh grapefruit	Sour	Dec. 11, 1930		.1025	.1450
Marsh grapefruit	Sour	Dec. 11, 1930		.1250	.....
Eureka lemon	Sweet	Oct. 3, 1930		.1300	.....
Eureka lemon	Sweet	Dec. 11, 1930		.1000	.1900
Eureka lemon	Sour	Oct. 3, 1930		.1213	.....
Eureka lemon	Sour	Oct. 3, 1930		.1125	.1563

The various plots received the different soil fertilizer treatments shown in table 7 and more fully discussed by Vaile (15). According to him the fertilization of the soil was started with relatively small amounts in 1907, the year the trees were planted. These amounts were gradually increased until 1914 when the plots received the following quantities annually until they were abandoned in July, 1933: 1.35 pounds actual nitrogen per tree; 2.70 pounds actual phosphoric acid per tree; and 1.35 pounds actual potash per tree. This means approximately 25 pounds per tree of 5–10–5 formula fertilizer (home-mixed) on the complete fertilizer plots, A and Q; 10 pounds of dried blood per tree on C and S; 9 pounds of nitrate of soda per tree on H; 14 pounds of steamed bone per tree on E, K, P; 2.5 pounds of sulfate of potash per tree on D, I, R; 13 pounds of superphosphate per tree on J; 8 cubic feet of manure per tree on V.

In table 7 the plots are arranged to correspond with the percentages of total phosphorus (P) in the healthy leaves. A study of the relation of the fertilizer

treatment to the percentages of phosphorus reveals the fact that the leaves of trees in plots V, C, Q, L, S, G, A, and H, which received the largest applications of nitrogen, contain the lowest percentages of phosphorus.

The data in table 7 show also the universality of the relation of higher percentages of phosphorus in mottled than in healthy leaves. Attention was directed in table 1 to the unusually high percentages of phosphorus in the

TABLE 7

Phosphorus content of gram aliquots of Valencia orange leaf samples obtained from trees of the Rubidoux fertilizer trials

PLOT	SOIL TREATMEMT	LEAF SAMPLES COLLECTED (1933)	PHOSPHORUS IN DRY MATTER OF LEAVES	
			Healthy	Mottled
			per cent	*per cent*
V	Manure, rock phosphate, and cover crop	Feb. 18	.1025	.1375
C	Dried blood	Jan. 10	.1100	.1575
Q	Complete: nitrate of soda, blood, superphosphate, and sulfate of potash	Feb. 16	.1125	.1475
L	Nitrate of soda, blood, and sulfate of potash	Feb. 3	.1138	.1550
S	Dried blood	Feb. 17	.1150	.1325
G	Nitrate of soda, blood, and bone	Jan. 12	.1188	.1400
A	Complete: sulfate of potash, nitrate of soda, blood and bone	Jan. 9	.1200	.1800
H	Nitrate of soda	Jan. 12	.1400	.2000
P	Bone	Feb. 16	.1375	.1550
K	Steamed bone and sulfate of potash	Feb. 3	.1413	.2000
N	Superphosphate and blood to equal N of bone plots	Feb. 15	.1450	.2125
T	No fertilizer	Feb. 18	.1450	.2200
R	Sulfate of potash	Feb. 17	.1550	.2200
D	Sulfate of potash	Jan. 10	.1625	.1850
B	No fertilizer	Jan. 10	.1850	.2150
M	No fertilizer	Feb. 15	.1988	.2225
I	Muriate, at first; later, sulfate of potash	Jan. 12	.2100	.2500
J	Superphosphate	Jan. 11	.2150	.2600
E	Steamed bone	Jan. 11	.2150	.2500

Valencia orange and lemon fruits from trees of plot H. In table 7 the Valencia orange leaves from this plot contain the highest percentages of phosphorus in the group of high nitrogen-fertilized plots.

The percentages of phosphorus are next highest in the bone plots, with the single exception of plot E, and in plot N, which received nitrogen to equal that of the bone plots. The highest percentages of phosphorus occur in the group (plots T to J inclusive) which either received no fertilizer (control) or no nitro-

gen. The data, therefore, according to the nitrogen received by the plots, may be divided into three groups, the nitrogen fertilizer treatments of which roughly correspond inversely to the percentages of phosphorus in the leaves. High percentages of phosphorus in healthy leaves are indicative, therefore, of a relatively reduced nitrogen supply. In mottled leaves the percentages of phosphorus roughly fall into the same three groups as do the healthy leaves except that the percentages are all on a higher level.

The data in table 7 make it clear that a determination of phosphorus is not of itself an adequate basis at all times for conclusions regarding the needs of the leaves for phosphate. Fraps (5) and others have questioned the reliability of existing chemical methods of determining soil deficiencies in ash constituents. The data in table 7 indicate the caution necessary in drawing conclusions and especially when diseased leaves are to be taken into account. From these data one might conclude that the dry matter of healthy leaves of the best trees contains 0.10 to 0.14 per cent of phosphorus. The trees in plots G and H, however, were in general badly mottled and in poor condition, whereas the trees in plot V were in excellent condition. Consequently, 0.10 per cent or even somewhat less may not constitute a phosphorus deficiency.

The association of increased percentages of phosphorus with the mottling of citrus leaves does not necessarily indicate a causal connection between the two factors. The use of dilute phosphoric acid in large sand cultures with Valencia orange trees produced a chlorosis that approached, but was not, a true mottle. Unfortunately these sand cultures were in asphalt-coated galvanized iron containers which may have contributed zinc as an interfering factor. Haas (7) previously has reported the effect of adding dilute phosphoric acid to Sierra loam soil in 12-gallon earthenware pot cultures in which Valencia orange trees were grown, but in which drainage was permitted. Such cultures were repeated again out-of-doors. No drainage was allowed to take place, and applications of calcium nitrate were made intermittently. The phosphoric acid solution was reduced in strength to 1, 2, and 3 cc. in 18 liters of distilled water and was applied from time to time; otherwise, distilled water alone was used. At the two higher strengths several, but not all, of the trees showed mottle-leaf with the leaves frequently of reduced size. As the experiment continued, the mottled areas burned and the tissue in the yellow areas contracted. This is illustrated in figure 2 of plate 1. No mottling developed in leaves collected from similar but control trees grown in soil that was irrigated with distilled water and treated occasionally with calcium nitrate solution.

In October, 1934, samples of such affected Valencia orange leaves were collected from trees in soil that received 3 cc. of phosphoric acid in 18 liters of distilled water. Analysis showed that such leaves contained 1.175 per cent of phosphorus in the dry matter, which is the highest value yet found in citrus leaves. This total phosphorus content consisted of 0.718 per cent of inorganic, 0.255 per cent of organic, 0.039 per cent of phospholipid, and the remainder of acid-insoluble phosphorus. The association of higher percentages of phos-

phorus with mottling in citrus leaves is of interest further because of the results obtained by Eidelman (3), who found that the chlorophyll content of plants varies approximately inversely with the phosphorus content.

Fractions in healthy and mottled leaves. Samples of healthy and mottled leaves of several varieties of citrus were collected on December 11, 1930, from trees grown in the pathology plots at the Citrus Experiment Station. Healthy and mottled leaves of a given variety were collected from the same trees. In some cases the mottled leaves were adjacent to the healthy leaves and in others somewhat distant from them. Each bracket in table 8 represents samples from the same group of trees. The percentages of inorganic, organic, and phospholipid phosphorus in the dry matter were determined and the results are presented in table 8.

TABLE 8

Phosphorus fractions of healthy and mottled citrus leaves

CONDITION OF LEAVES	SCION	ORANGE STOCK	PHOSPHORUS AS PER CENT OF DRY MATTER		
			Inorganic	Organic	Phospholipid
Healthy	Washington navel orange	Sweet	.125	.078	.018
Mottled	Washington navel orange	Sweet	.155	.096	.015
Healthy	Washington navel orange	Sweet	.138	.043	.017
Mottled	Washington navel orange	Sweet	.165	.057	.016
Healthy	Valencia orange	Sweet	.121	.065	.010
Mottled	Valencia orange	Sweet	.142	.078	.016
Healthy	Eureka lemon	Sweet	.095	.030	.009
Mottled	Eureka lemon	Sweet	.131	.036	.013
Healthy	Marsh grapefruit	Sour	.088	.039	.005
Healthy	Marsh grapefruit	Sour	.085	.022	.008
Mottled	Marsh grapefruit	Sour	.113	.035	.009

The percentages of inorganic phosphorus exceed in every case the sum of those of the organic and phospholipid fractions. Larger percentages of inorganic and organic phosphorus are clearly shown to occur in mottled leaves. With the exception of the percentages for Washington navel orange the percentages of phospholipids also were higher in the mottled leaves. The large preponderance of phosphorus in the inorganic form in citrus leaves makes its availability the greater to tissues in need of this element. The relatively low percentages of organic phosphorus are of interest because, in studies to be reported (9), it was found that there is a poor utilization of organic phosphorus by citrus unless the inorganic phosphorus supply is very low and that the phosphorus absorbed by citrus is largely in the inorganic form. It is desirable to know whether there are large differences in the total phosphorus content,

not only in the leaves and fruit, but also in the bark of trees in the field. Data in this regard do not exist. In studies of phosphorus deficiency it is essential that such basic data for healthy trees be available. Certain trees in the field at the Citrus Experiment Station which were about to be removed were used for such a study.

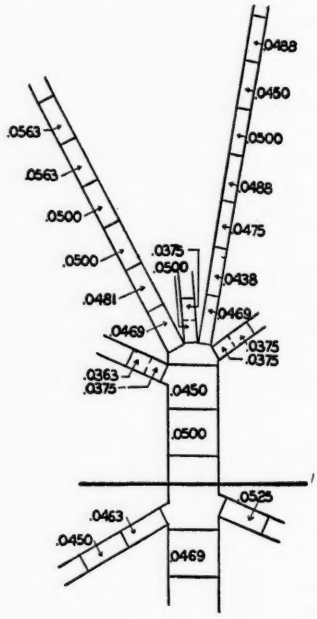

FIG. 2

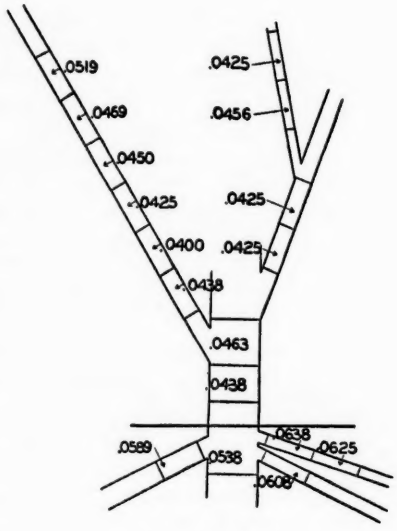

FIG. 3

FIG. 2. DIAGRAMMATIC REPRESENTATION OF THE PHOSPHORUS CONTENT (PER CENT IN DRY MATTER) OF 1-FOOT LENGTHS OF BARK OBTAINED FROM A VILLAFRANCA LEMON TREE ON SOUR ORANGE ROOTSTOCK GROWN IN THE FIELD AT THE CITRUS EXPERIMENT STATION

The tree was planted in June, 1917, and the circles of bark were cut on October 31, 1928. The heavy horizontal line designates the surface of the soil.

FIG. 3. DIAGRAMMATIC REPRESENTATION OF THE PHOSPHORUS CONTENT (PER CENT IN DRY MATTER) OF 1-FOOT LENGTHS OF BARK OBTAINED FROM A LUE GIM GONG ORANGE TREE ON SOUR ORANGE ROOTSTOCK GROWN IN THE FIELD AT THE CITRUS EXPERIMENT STATION

The tree was planted in 1919, and the circles of bark were cut on October 31, 1928. The heavy horizontal line designates the surface of the soil.

Phosphorus in citrus bark. Determinations were made of the percentages of total phosphorus in the dry matter of the bark of Villafranca lemon trees. The results are diagrammatically represented in figure 2. The large 6-foot branch to the left in the figure shows values which increase slightly toward the tip;

the values for the sections from the 7-foot branch to the right show no definite trend, nor do the percentages for the trunk or rootstock. The several short branches show some of the smallest values. In general there is a fair degree of uniformity in the percentages of phosphorus in the bark of the trunk and largest branches and that of the large divisions of the rootstock.

Bark was also obtained from a Lue Gim Gong orange tree on sour orange rootstock. The percentages of phosphorus in the various 1-foot wide circles of bark are diagrammatically represented in figure 3. The values for the rootstock bark exceed those of the trunk and branches of the top. The 6-foot branch to the left in the figure shows a slight increase in the percentages in a direction toward the tip of the branch. These results show the relatively uniform distribution of phosphorus throughout the bark of the tree. This may be considered as indicative of the saturation of these tissues with phosphorus and of the storage of any excess in the leaves and youngest roots.

Bark samples were also collected from the trunks of orange trees grown on the plots of the Rubidoux fertilizer trials. Observation was made of the condition of the trees as regards mottle-leaf and of the manner of cleaning the bark prior to the removal of the bark samples. The samples were taken from the trunks about 6 inches above the bud union. The percentages of total phosphorus in the dry matter of the bark are remarkably uniform (0.0356 to 0.0463) regardless of the treatment of the samples during their collection. The bark of mottled trees showed no increased percentages of phosphorus, nor was there a relation of the percentages to the soil fertilizer treatment. The data suggest that the bark tissue is saturated with phosphorus.

In another study the percentages of total phosphorus were determined in the dry matter of the bark of sour orange rootstocks of young nursery trees that were budded to Washington navel orange.

One lot of trees was badly mottled. One group of 17 roots and another of 16 roots of the mottled trees were brushed free of soil while dry. The percentages of phosphorus found in the dry matter of this bark were 0.0750 and 0.0875, respectively. In another group of 15 roots of this same lot the rootstocks were first washed with tap water to remove adhering soil and then with distilled water. The percentage of phosphorus in the bark of this group was 0.0858.

A second lot of similar trees was obtained in which no mottling was evident. The bark of one group of 17 rootstocks that were brushed while dry contained 0.0829 per cent of phosphorus and that of another group of 16 rootstocks that were washed with tap water and then with distilled water contained 0.0900 per cent.

In these samples obviously the finest rootlets were not used because they could not be thoroughly cleaned and because the bark could not be separated. The data for the bark of these rootstocks showed a uniformity in the percentages of phosphorus, as did the bark from the trunks of older trees.

A study of the bark of the trunk of 3-year-old Rough lemon seedlings grown in soil showed some variations in the phosphorus content of the dry matter.

The bark of the shoots contained 0.0800 to 0.0825 per cent; that of the trunk: last elongation, 0.1200 per cent, upper half of remainder of trunk, 0.1100 per cent, lower half, 0.0925 per cent; that of main tap roots, 0.1175 per cent; and that of large lateral roots, 0.1063 per cent.

In January, 1927, analyses were made of the phosphate in the sap obtained by air suction from branches of Washington navel orange trees. The ash showed for mottled trees 41 p.p.m. and for healthy trees 43 p.p.m. phosphate, again revealing a uniformity.

SUMMARY

The phosphorus content and its relation to other constituents of various portions of citrus trees were investigated.

Lemon flowers contain the highest percentage of phosphorus of any stage in the fruiting process. The percentage of phosphorus in the dry matter of lemons (not tree-ripe fruit) shows a decrease with increasing maturity of the fruit. The content of phosphorus (grams) per average lemon fruit becomes greater with increasing maturity of the fruit. After the lemon fruits become a certain size or have a given dry weight the phosphorus content (grams) of the lemons from Riverside exceeds that of fruits from Santa Barbara. Lisbon lemons of a given degree of size or dry weight contain less phosphorus than Eureka lemons grown under the same environmental conditions.

The dry matter of the peel of lemons contains a higher percentage of phosphorus (average 0.1366) than that of the peel of oranges (average for Valencia orange peel 0.0709 and for Washington navel orange peel 0.0772).

If averages are considered, the percentage of phosphorus in the dry matter of Valencia orange pulp was 0.1853, in Washington navel orange pulp 0.1958, and in lemon pulp 0.2390. The same general relation found in the peel holds also in the pulp.

Valencia orange and lemon peel or pulp from fruits of plot H, which received nitrate of soda as its fertilizer treatment, contained markedly higher percentages of phosphorus than the peel or pulp of fruit from any trees of the other plots.

In the absence of phosphorus in the culture solution the percentages of that element in the dry matter of Valencia oranges were between 0.0519 and 0.0575 for ripe fruit and slightly higher for smaller green fruit; when the culture solution contained 105 p.p.m. phosphate, the percentage was 0.2125.

The outer portion of the dry matter of the peel of oranges contains a greater percentage of phosphorus than the inner portion in both the stem and tip halves. The values for the tip halves exceed those for the stem halves.

Phosphorus-free culture solutions permitted the growth of orange fruits but produced a marked reduction in the percentage of phosphorus in the dry matter of the peel as compared with nearly ripe fruit grown on cuttings in complete culture solution.

The phosphorus fractions in Valencia orange peel follow the same direction as was found for the oil of Valencia orange peel.

Analysis of healthy citrus leaves from trees in the field showed the dry matter of Eureka lemon leaves to contain 0.0900 to 0.1656 per cent of phosphorus; Lisbon lemon leaves, 0.0950 to 0.1875 per cent; Washington navel orange leaves, 0.1125 to 0.1250 per cent; and Valencia orange leaves, 0.0750 to 0.1250 per cent.

Mottled citrus leaves in every case contained markedly higher percentages of phosphorus than healthy leaves.

Healthy leaves of trees in plots that received the largest applications of nitrogen contain the lowest percentages of phosphorus. In healthy leaves high percentages of phosphorus are indicative of a relatively reduced nitrogen supply. The percentages of phosphorus in mottled leaves roughly fall into the same groups as do those in the healthy leaves, except that they are all on a higher level. Determinations of phosphorus in leaves are not of themselves adequate bases at all times for conclusions regarding the needs of the leaves for phosphate.

The percentages of inorganic phosphorus in citrus leaves exceed in every case the sum of those of the organic and phospholipid fractions.

There is a fair degree of uniformity in the percentages of phosphorus in the bark of the trunk and largest branches of a Villafranca lemon tree and in that of the larger subdivisions of the rootstock (sour orange). Data obtained in regard to the phosphorus content of healthy and mottled trees of plots of the Rubidoux fertilizer trials also show a marked uniformity and suggest that there is a saturation of the bark tissue of these mature trees with respect to phosphorus.

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PLATE 1

FIG. 1. Healthy growth of citrus cutting in culture solution without aeration in 21-quart shallow Swedish enamel ware pan. Valencia orange leafy-twig cutting as scion on Rough lemon leafy-twig cutting as stock. Culture solution contained 105 p.p.m. of phosphate for only a few days at intervals of several weeks. When phosphate was absent, 5 p.p.m. of aluminum was used. Iron, boron, and manganese are the only traces of elements added to the regular culture solution. Zinc was not added. Note the presence of a cluster of five large oranges and the absence of any mottling.

FIG. 2. Phosphate in relation to mottle-leaf. Valencia orange leaves from trees in Sierra loam soil cultures in 12-gallon earthenware pots without drainage. Calcium nitrate solution was occasionally added to permit healthy growth, as shown by the leaf at the left in the upper row. One to three cubic centimeters of phosphoric acid, diluted with distilled water to 18 liters, was occasionally added to certain cultures. In several of such cultures mottle-leaf developed, and as the leaves became fully mature the mottled areas began to dry out or burn.

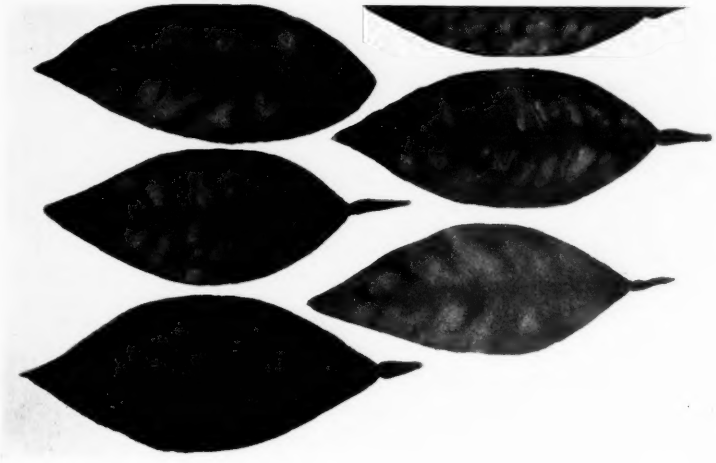

FIG. 2

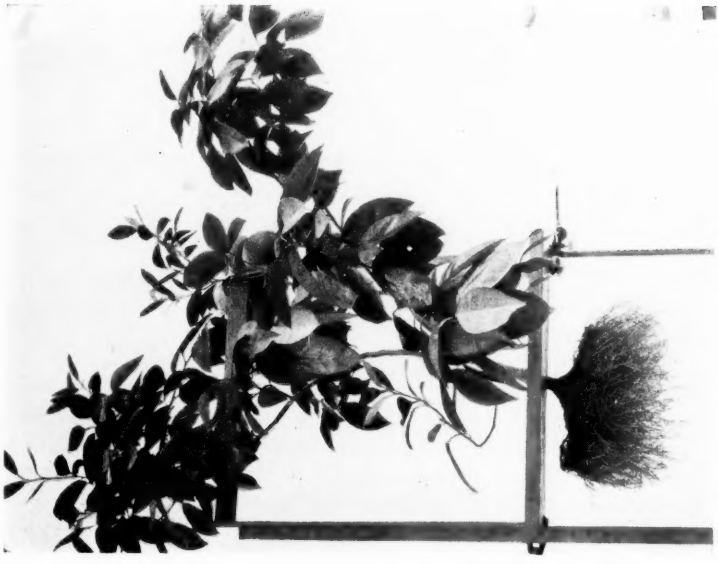

FIG. 1

UNIV. OF MICH.

HYDRATION OF MINERALS AND SOIL COLLOIDS IN RELATION TO CRYSTAL STRUCTURE[1]

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Investigators have classified soil water as hygroscopic, water of hydration, adsorbed water, osmotic water, water of swelling, imbibed water, and various other types. Of course these terms are not meant to indicate that there are various kinds of water such as "heavy water" and "light water"; they are merely expressions of different relations that exist between the solid and the liquid phase. Strictly speaking, the numerous categories of soil water are vague designations or descriptions of the various forces which come into play in the process of water adsorption or hydration.

For a better understanding of soil-water relations in general, it becomes necessary to learn more about the specific surface forces which are characteristic of solids and which are able to attract water molecules. Since the present study is a first attempt in this direction, some of the conclusions are necessarily of tentative nature.

The colloids represent one of the most effective constituents of soils for water adsorption. Unfortunately, relatively little is known of these important substances, particularly in respect to the nature of their surfaces. It would appear to be hopeless to speculate about the absorptive forces of unknown surfaces, but the following mode of approach seems to be promising. By investigating the water relations of minerals of known composition and crystal structure and comparing the results with those obtained with soil colloids, one might then be able to interpret the hydration of the colloidal particles by way of analogy.

SIGNIFICANCE OF VAPOR PRESSURE AND TEMPERATURE

If a dry surface is exposed to an atmosphere containing water molecules, the latter will strike the surface at random. If the surface contains attractive forces, some of the water molecules will be held and temporarily may stick to the surface. The greater the number of water molecules in the gas space, that is, the higher the vapor pressure, the more probable this mode of absorption will be. Evidently a strict control of the vapor pressure is essential in a study of water adsorption from the gaseous state.

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Because of thermal agitation, the absorbed water molecules gradually escape again from the surface; for a given vapor pressure, this reverse process is the more pronounced the higher the temperature. Thus, temperature is another important variable in hydration studies.

In the present study, the vapor pressure was kept constant while the temperature was varied from 25° to 800°C. A relatively low vapor pressure (50 per cent H_2SO_4) was selected in order to avoid ordinary water condensation, which would obscure the rôle played by the true surface forces of the solid.

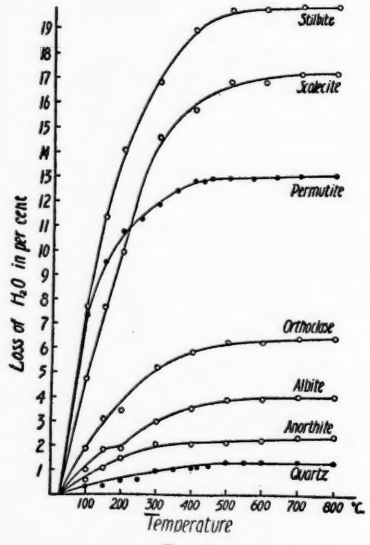

FIG. 1

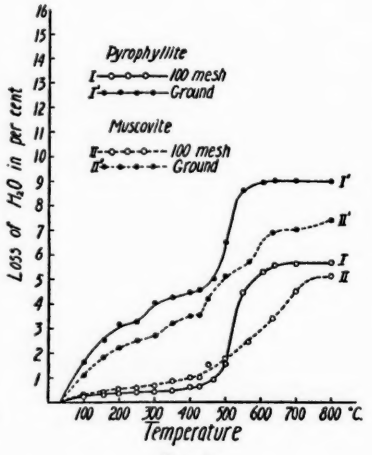

FIG. 2

FIG. 1. DEHYDRATION CURVES OF MINERALS OF THE LINKED TETRAHEDRA TYPE (FELSPAR TYPE)

In the case of quartz and felspars the position of the flat branch of the curve is not a characteristic of the mineral but depends on the degree of fineness.

FIG. 2. DEHYDRATION CURVES OF PYROPHYLLITE AND MUSCOVITE

In the 100-mesh samples the vertical branch (at 500°C.), which indicates crystal lattice water, is very pronounced.

EXPERIMENTAL METHOD

The materials used in this investigation were first ground as indicated hereinafter and then brought to equilibrium with the atmosphere above 50 per cent H_2SO_4 at a constant temperature of 25°C. The dehydrations were carried out against a similar atmosphere which was maintained by passing a current of air first through a series of towers containing 50 per cent H_2SO_4 and then through the electric oven. The temperature was controlled by means of a thermocouple placed in close proximity to the crucibles in which the samples were held.

Approximately 1-gm. samples were used in duplicate and were kept at each temperature until loss in weight ceased.

DEHYDRATION CURVES OF SELECTED MINERALS

Figure 1 shows a family of curves, the members of which are nearly alike in shape. This group includes *quartz*, several *felspars*, two *zeolites*, and a *permutite*. Should the curve for a good-sized felspar crystal be plotted, it would run so close to the X-axis that it could not be shown on the scale chosen. The

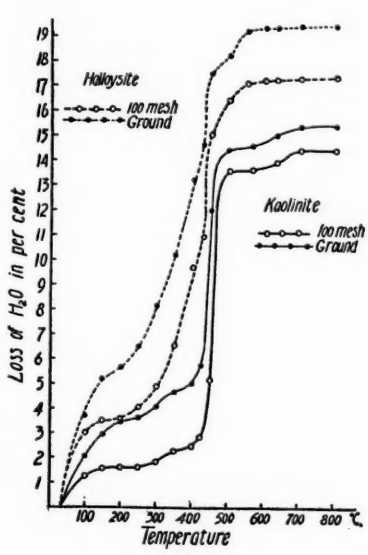

FIG. 3

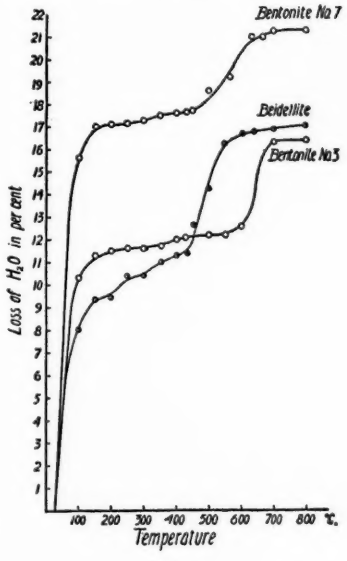

FIG. 4

FIG. 3. DEHYDRATION CURVES OF KAOLINITE AND HALLOYSITE

In the case of kaolinite note the extended vertical branch which corresponds to the water of crystallization.

FIG. 4. DEHYDRATION CURVES OF BEIDELLITE AND BENTONITES

The curves suggest the presence of adsorbed, as well as crystal lattice, water.

increased surface area caused by grinding the crystal shifts the dehydration curve upwards in proportion to the intensity of grinding. The fact that grinding increases the surface area can also be ascertained by measuring the increase in base-exchange capacity and the size of the particles (with sedimentation methods and the ultra-microscope). The end point (flat branch of curve) for all these curves is directly proportional to the base-exchange capacity. This clearly indicates that an increase in surface proportionally augments the water content of the substances; this water must have come from the atmosphere to which the minerals were exposed. Most of the water is given off below 400°C.

We shall designate this type of water as *adsorbed water*, or more specifically, *felspar water*. The relative rate of loss of the adsorbed water is the same for all the substances, which indicates that the same kind of adsorption forces are active on their exposed surfaces.

A different type of dehydration curve is given by the *micas* and *pyrophyllite* (fig. 2). The curves ascend gradually, and at the higher temperatures (above 500°C.) a marked loss of water occurs within a relatively narrow temperature interval. This pronounced change is commonly explained as escape of *crystal lattice water*.

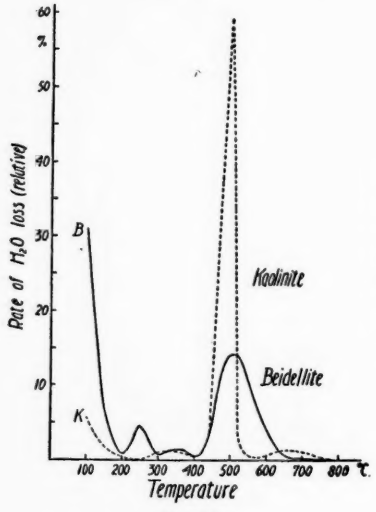

FIG. 5

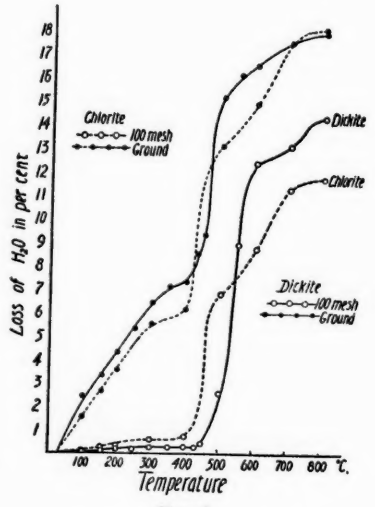

FIG. 6

FIG. 5. GRAPHS SHOWING THE EXPLOSION-LIKE LOSS OF CRYSTAL LATTICE WATER
Relative losses per 50°C. intervals

FIG. 6. DEHYDRATION CURVES OF DICKITE AND CHLORITE
As in previous graphs, grinding increases the total water content but reduces the length of the vertical branch of the curve.

Kaolinite also exhibits in the curve a pronounced break, even more striking than that of muscovite (fig. 3). The inflection point occurs at a lower temperature, and the amount of the vertical shift in the curve is about twice as great as in mica, indicating a greater amount of water of crystallization. It is interesting to note that the dehydration curves for both kaolinite and halloysite agree well with those published by Ross and Kerr (10, 11).

An entirely different curve is given by the *bentonites* and *beidellite* (fig. 4). In a certain way the curves of these clays can be considered as combinations of types already discussed. There are, first, a pronounced water loss at moder-

ately low temperatures, which suggests the presence of adsorbed water, and second, an inflection point above 400°C., which is a strong indication of the presence of crystal lattice water. These curves will be of special significance in the study of soil colloids.

The curves presented in figure 5 merely represent a different way of plotting the data of kaolinite and beidellite previously shown. The lines show relative rates of water loss. The percentage of the total water lost for each increase in temperature of 50°C. was plotted against temperature. This mode of illustration brings out forcefully the explosion-like loss of crystal lattice water. According to modern concepts of crystal structure, the water molecules of these substances exist as OH ions and constitute an essential part of the lattice. High temperatures increase the thermal agitation to such a degree that the water molecules virtually jump out of the lattice with a consequent destruction

TABLE 1

Differentiation of total water content of minerals into adsorbed and crystal lattice water (anhydrous basis)

MINERAL	TOTAL WATER	ADSORBED WATER	CRYSTAL LATTICE WATER
	per cent	*per cent*	*per cent*
Muscovite	5.37	1.04	4.33
Pyrophyllite	6.00	0.64	5.36
Dickite	16.65	0.49	16.16
Kaolinite	16.86	2.80	14.00
Ca-Bentonite No. 3	19.65	14.59	5.06
Ca-Beidellite	20.57	13.59	6.98
Halloysite	20.91	4.29	16.62
Ca-Bentonite No. 7	27.09	22.49	4.60

of the crystal. The shattering of the mineral and the possible rearrangement of the atoms have been verified by X-ray methods.

Table 1 summarizes the content of crystal lattice water and adsorbed water in various minerals. It should be noted that the common minerals contain more lattice water than adsorbed water, whereas the bentonitic substances contain a much greater proportion of adsorbed water.

EFFECT OF GRINDING

Figure 6 shows the effect of increased specific surface on the hydration properties of *dickite* and *chlorite*. Dickite, ground to pass a 100-mesh sieve, yields a curve very similar to that of kaolinite (Ross and Kerr, 10). Upon further grinding, the total water content increases, as seen from the shift of the curve at 800°C. (14 → 18 per cent H_2O). This is properly explained as an increase in adsorbed water due to greater specific surface area. It is of interest to note, however, that the extent of the vertical section has been changed; it appears

that the amount of crystal lattice water has been reduced. In addition, the position of the inflection point has been shifted to a lower temperature.

In figure 7, the data for *pyrophyllite* and *felspar* are plotted as relative percentages on an anhydrous basis. The coarse pyrophyllite loses about 90 per cent of its total water above 400°C., and the steep slope clearly indicates crystal lattice water. Grinding has produced two significant changes. First, the inflection point has been shifted to a lower temperature, indicating that crystal lattice water escapes more readily from the interior of small particles than from large ones. We are of the opinion that this influence of particle size constitutes an important feature in the interpretation of the dehydration curves of soil colloids. Differences in the inflection points do not necessarily signify different lattices but may be the result merely of variations in particle size.

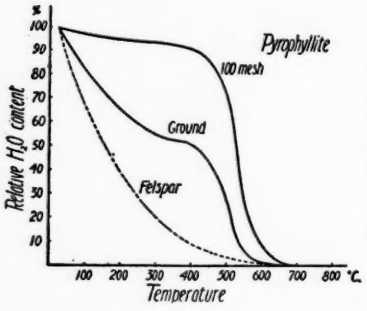

Fig. 7

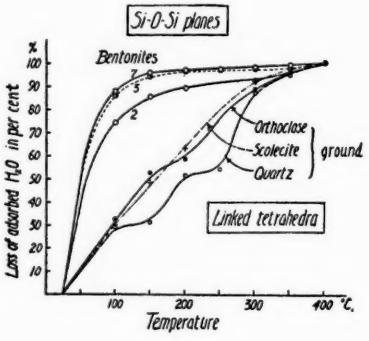

Fig. 8

Fig. 7. Relative Water Content on Anhydrous Basis

Ground pyrophyllite occupies a position intermediate between coarse pyrophyllite and ground felspar.

Fig. 8. Differentiation of Adsorbed Water into Felspar and Bentonitic Types of Adsorbed Water

Another result of grinding is the apparent reduction of crystal lattice water to 50 per cent as contrasted with 90 per cent before grinding. The difference appears as adsorbed water, that is, it is given off at lower temperatures. A plausible explanation is the following: In the interior of the lattice the OH ions are surrounded by other atoms or ions and the escape of H_2O is difficult. If the OH ions are brought to the surface by way of grinding, they are held by the particle on one side only, they experience more freedom of movement, the extent of thermal agitation is greater, and they can escape at lower temperatures. In fact, it is very difficult to distinguish between adsorbed water and surface crystal lattice water in such instances. For comparison, the felspar curve has been plotted, and it is evident that further reduction of particle size would tend to bring the pyrophyllite curve even closer to the felspar line. The

important conclusion follows that in the range of colloidal dimensions the fundamental classification of minerals as anhydrous and hydrous loses some of its significance because the superficial crystal lattice OH ions act as adsorbed forms of water.

Table 2 gives a summary of the effect of increased specific surface. In all cases (except permutite), grinding increased the total water. In the case of hydrous minerals, grinding increased the amount of adsorbed water more than the total water, which was caused by crystal lattice water coming off below 400°C. Correspondingly, the amount of crystal lattice water, as found in coarser particles, was reduced. It should be remembered that we designate lattice water as that portion of total water which comes off at the beginning of

TABLE 2

Changes in total adsorbed and crystal lattice water as a result of increased specific surface area (anhydrous basis)

MINERAL	ADSORBED ION	INCREASE IN SATURATION CAPACITY	INCREASE IN TOTAL WATER	INCREASE IN ADSORBED WATER	DECREASE IN LATTICE WATER
		m.e. per 100 gm.	*gm. per 100 gm.*	*gm. per 100 gm.*	*gm. per 100 gm.*
Hydrous minerals:					
Muscovite	K	38	2.56	2.69	0.13
Dickite	H	39	5.12	8.45	3.33
Kaolinite	H	40	1.32	3.05	1.73
Bentonite No. 3	Ca, H	42	3.44	4.12	0.68
Pyrophyllite	H	80	3.94	4.28	0.34
Beidellite	Ca, H	151	0.75	2.19	1.44
Anhydrous minerals:					
Permutite	Ca	0	−0.03	−0.03	....
Quartz	H	3	0.62	0.62	....
Orthoclase	K	2	2.01	2.01	....
Biotite	K	53	3.92	3.92	....

the vertical branch of the curve, regardless of whether this amount is greater or smaller than the theoretical lattice water content of the ideal mineralogical formula.

PROPERTIES OF ADSORBED WATER

It seems desirable to discuss in greater detail the nature of the adsorbed water. For this purpose we have disregarded the lattice water and have set the total adsorbed water equal to 100. We shall call "adsorbed water" that proportion of total water which comes off at 400°C., provided there is no evidence that true crystal lattice water is included in this category.

In figure 8, the relative loss of adsorbed water has been plotted against temperature. Two groups of curves appear to be prominent: First, the felspar, zeolite, and quartz lose their adsorbed water at a relatively uniform, but low

rate; secondly, the bentonites exhibit a strong bend in the curves, showing that the greatest fraction of their adsorbed water is lost at temperatures below 100° or 150°C. It seems that in general the adsorbed water is made up of different forms, and one might speak of *felspar* and *bentonitic types of adsorbed water.*

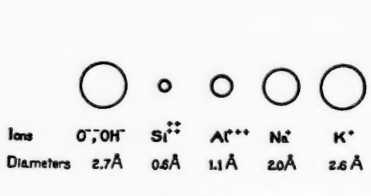

FIG. 9

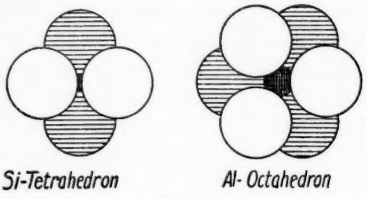

FIG. 10

FIG. 9. SIZE OF IONS AS FOUND IN CRYSTALLIZED ALUMINO SILICATES
Si should be 0.8Å instead of 0.6 as shown

FIG. 10. BUILDING STONES OF ALUMINO SILICATES
The large circles represent oxygen ions, the small ones silicon or aluminum ions.

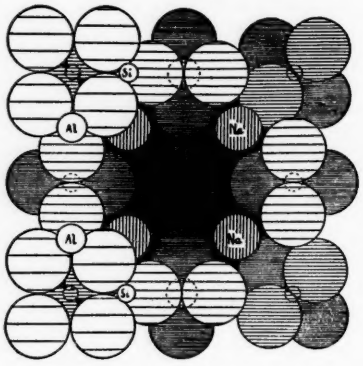

FIG. 11

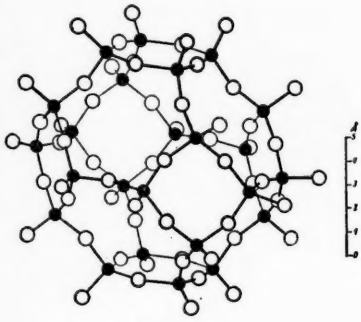

FIG. 12

FIG. 11. STRUCTURE OF ULTRAMARINE
The large circles are oxygen ions [After Jaeger (5)]

FIG. 12. SCHEMATIC NETWORK OF ULTRAMARINE
The broken bonds on the surface are shown [After Jaeger (5)]

The explanation is revealed by a study of the crystal structure of these substances. The one group (felspars, etc.) is made up of linked tetrahedra, whereas the bentonites are characterized by Si-O-Si planes. To explain these classifications fully it becomes necessary to discuss briefly modern concepts of crystal lattices.

THE STRUCTURE OF ALUMINO SILICATES IN RELATION TO ADSORBED WATER

According to the viewpoint of Bragg (2), Goldschmidt (3), Pauling (8, 9), and others, alumino silicates are made up of electrically charged particles which act as impenetrable spheres and which are properly called "ions." The *radii of the ions* are known (fig. 9). Attention is called to the important fact that O ions are the largest whereas Si and Al ions are so small that they can occupy the interstice in the center of four closely packed oxygen ions as shown in figure 10. Si or Al ions thus located are referred to as *silicon tetrahedra* or *aluminum tetrahedra*. In certain alumino silicates the Al ion is surrounded by six O ions; this "radical" is called an *aluminum octahedron*. Si and Al tetrahedra and Al octahedra are the building stones of alumino silicates, and the various structures are the results of variations in the arrangement of these ionic clusters.

Definition of broken-bond water

Figure 11 shows the arrangement, according to Jaeger (5), of tetrahedra in the case of *ultramarine*, a mineral related to the zeolites. The Al and Si ions are clearly recognizable. In the interior is seen a large cavity, which is the seat of the exchangeable ions (Na) and of loosely held water molecules (6). The same structure is shown in a more schematic manner in figure 12 in order to depict the three-dimensional linking of the tetrahedra. The black circles are Al or Si ions, the white circles indicate O ions. Every O ion is linked to two Si or Al ions. It is not possible to cut across the lattice without breaking the linkages, and it is clearly seen that the exposed ions possess a free "bond." We are of the opinion that the free bonds (Al, Si, O), which are the centers of strong electric fields, are responsible for the attraction of water molecules and thus constitute one type of adsorption force.

Water molecules are dipoles, that is, molecules in which the positive and negative charges are unsymmetrically arranged, and it is by virtue of this fact that they are strongly attracted by ions through the process of polarization and orientation. This type of linkage is relatively strong: considerable energy is necessary to disrupt it. We believe that such attraction is of major importance in the case of felspars which are considered to have linked tetrahedra structures. Tentatively we shall designate the felspar type of adsorbed water as "*broken-bond water*."

Definition of planar water

Other arrangements of tetrahedra are possible. Of special significance are the so-called "Si-O-Si planes" (oxygen planes), which are made up of rings consisting of six linked tetrahedra. Figure 13 shows such a plane as viewed from below. Theoretically, the area of such a sheet can be infinitely great. The most characteristic feature of an Si-O-Si plane, or of an OH-Al-OH plane, is the absence of unsaturated valences or free electric fields. In the plane itself there are no broken bonds and consequently no pronounced centers of

attraction. Nevertheless, the weak electric stray fields which are always present are able to attract water molecules. One would expect this form of adsorbed water to be loosely held and easily given off at low temperatures. We shall designate such adsorbed water as *planar water*.

Figure 14 shows the crystal structure of *kaolinite* and *montmorillonite* according to Hofmann, Endell, and Wilm (4). Note the existence of O^{--} and OH^{-} planes in these minerals. At the edges the planes are cut, and broken bond occur. The colloidal particles are built of a series of such plane packages.

Figure 15 gives a schematic picture of the *hydration conditions of a Si-O-Si plane*. The white circles denote O ions; the small black ones, Si ions within the tetrahedra. On the right, the plane is cut off, and free electric fields of O and Si ions attract water molecules (black circles), giving rise to broken-bond

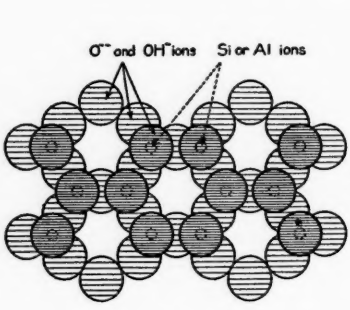

FIG. 13

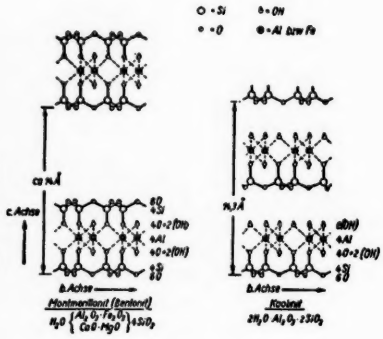

FIG. 14

FIG. 13. NEUTRAL O AND OH PLANE SEEN FROM BELOW

FIG. 14. CRYSTAL STRUCTURE OF KAOLINITE AND MONTMORILLONITE

The lattice dimensions are correct, but the ion sizes are not drawn to scale. [After Hofmann, Endell, and Wilm (4).]

water. On the surface of the sheet we have the loosely attracted planar water (black circles). According to this viewpoint a substance consisting of planes has both broken bond and planar water, the relative proportion of the two depending on the shape of the particle. If the disintegration should take place mainly parallel to the planes, planar water would dominate; on the other hand, if grinding should break the particles chiefly across the planes, broken-bond water would exceed the planar water.

Table 3 presents a tabulation of broken-bond and planar water. The data indicate the percentages of adsorbed water given off at 150°C. All the materials referred to here were Ca-saturated at the outset in order to eliminate any possible variation due to the hydration effect of the adsorbed ion. The first two columns give the values for the felspars, in which less than 50 per

cent of the total adsorbed water is lost at 150°C., indicating that the adsorbed water molecules are held tightly. These figures are characteristic of broken-

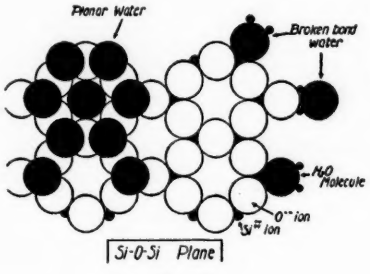

FIG. 15

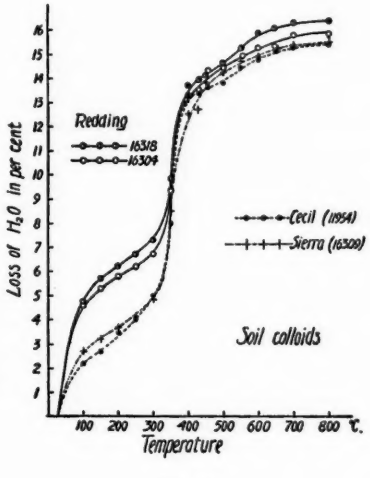

FIG. 16

FIG. 15. HYDRATION OF A NEUTRAL Si-O-Si PLANE

The white circles represent oxygen ions; the small black circles, silicon ions; and the large black circles, adsorbed water molecules.

FIG. 16. DEHYDRATION CURVES OF REDDING, CECIL, AND SIERRA SOIL COLLOIDS

The SiO_2/Al_2O_3 ratio is 2 or less

TABLE 3

Per cent of adsorbed water lost at 150°C.

BROKEN-BOND WATER		PLANAR WATER		MIXTURES	
Mineral	H_2O	Mineral	H_2O	Mineral	H_2O
	per cent		*per cent*		*per cent*
Albite II	34.2	Bentonite No. 8	85.4	Biotite	55.1
Labradorite	38.6	Bentonite No. 2	85.6	Muscovite	56.1
Anorthite	44.0	Bentonite No. 6	88.5	Pyrophyllite	61.2
Albite I	45.4	Bentonite No. 7	89.2	Kaolinite I	67.1
Orthoclase	47.8	Bentonite No. 3	90.3	Kaolinite II	47.8
Oligoclase	49.0	Beidellite	92.2	.....	....
.....	....	Bentonite No. 3a	93.0	.....	....
.....	....	Bentonite No. 7a	95.8	.....	....

bond water. The middle columns represent planar water. It will be noted that in this case from 85 to 96 per cent of all adsorbed water leaves the surface at 150°C., a fact which points toward the dominance of very weak physical or

chemical bonds. Bentonite and beidellite are typical examples of this group of substances. The last set of columns comprises intermediate cases. Here the areas of the planes and the broken lattices are of similar magnitude and the hydration values fall between the two categories.

DISCUSSION OF SOIL COLLOIDS

The study of hydration and dehydration of minerals of known structure has revealed the following facts: First, it is possible to evaluate the amount of crystal lattice water and its critical temperature of escape; secondly, the amount of adsorbed water can be determined; and thirdly, the water of adsorp-

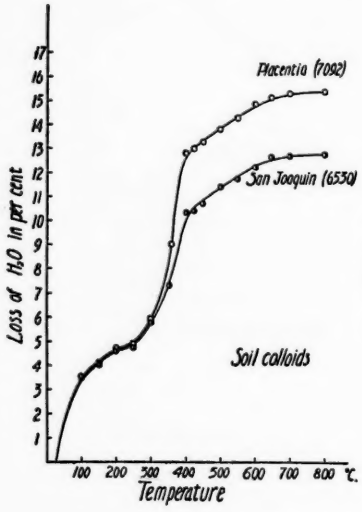

FIG. 17

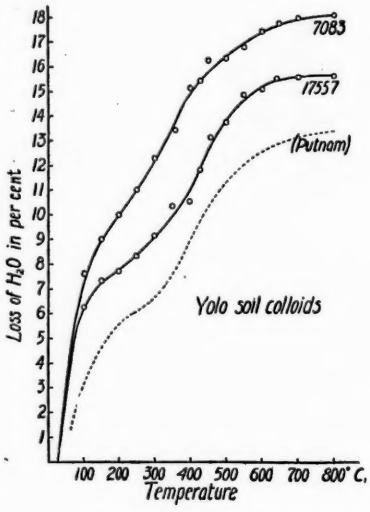

FIG. 18

FIG. 17. DEHYDRATION CURVES OF PLACENTIA AND SAN JOAQUIN SOIL COLLOIDS

FIG. 18. DEHYDRATION CURVES OF YOLO COLLOIDS

The SiO_2/Al_2O_3 ratio is approximately 3

tion can be divided into broken-bond and planar water. The question arises as to whether soil colloids exhibit similar relations. Accordingly, about 40 different soil colloids (1 micron or less) were saturated with Ca and then subjected to the same technique as the minerals already discussed. The results are typified by figures 16, 17, 18, and 19.

Redding, Cecil, Sierra. Figure 16 illustrates four soil colloids of reddish color and low SiO_2-Al_2O_3 ratios. The Cecil, from Alabama, and the Sierra, from California, were derived from acid igneous rocks and, though they were formed several thousand miles apart, they are practically alike in their dehydration properties. A steep vertical branch is evident, and suggests the pres-

ence of crystal lattice water. It should be noted that the critical temperature at which lattice water escapes is below 400°C.

Placentia, San Joaquin. Colloids were isolated from strongly weathered alluvial deposits in California (fig. 17). The two soil types are supposed to be genetically related, the San Joaquin being the more mature. In regard to adsorbed water the two colloids are identical, the main difference being shown by the length of the vertical branch of the crystal lattice water curve.

Yolo colloids. Of very different nature are the Yolo colloids of California, which appear to be related to the Putnam colloids of Missouri (1) (fig. 18). A smooth, wave-like shape is typical for these dehydration curves. The presence of crystal lattice water is indicated by the inflection point, but the escape

TABLE 4

Adsorbed water and crystal lattice water in soil colloids (anhydrous basis)

COLLOID	LABORATORY NUMBER	TOTAL WATER	ADSORBED WATER	CRYSTAL LATTICE WATER
		per cent	*per cent*	*per cent*
Cecil	11954	18.04	4.74	13.30
Sierra	16309	18.19	4.81	13.38
Redding	16318	19.40	8.01	11.39
Redding	16304	18.69	7.22	11.47
San Joaquin	6530	14.54	5.41	9.13
Placentia	7092	18.03	5.74	12.29
Yolo	7083	21.83	12.12	9.67
Yolo	17557	18.25	10.53	7.72
Susquehanna A	16312	19.12	10.61	8.51
Susquehanna B	16313	21.07	14.01	7.06
Susquehanna C (10–20 inches)	17554	20.75	13.39	7.36
Susquehanna D (10 feet)	17555	21.08	14.12	6.96
Susquehanna E (11 feet)	17556	29.29	23.61	5.68
Putnam	.....	15.30	7.25	8.05

of the lattice water appears to be less violent than in the case of the previous colloids.

Table 4 shows a series of soil colloids tabulated according to their crystal lattice water and adsorbed water. Generally speaking, the total water content of these colloids is high; this fact is undoubtedly related to the small particle size and consequent great specific surface. As in the case of the minerals, two groups can be recognized; namely, those colloids which have more crystal lattice water than adsorbed water (Cecil type), and those in which this relation is reversed (Yolo, Susquehanna).

Susquehanna profile. Of great interest are the curves of the Susquehanna colloids (fig. 19) which were extracted from a Susquehanna profile located in the southeastern United States (Alabama). The curve of the so-called E-horizon (11 feet in depth), stands apart from the others of this profile; a comparison

with the curves for the minerals clearly points toward a very close resemblance to bentonite. The remaining curves form a uniform family with regular alterations according to depth. The higher the base-exchange capacities, the steeper the initial slope of the curves. The presence of lattice water is beyond doubt, if analogies are at all justified.

NATURE OF SURFACE OF CLAY PARTICLES

Table 5 contains various data of considerable significance. In column 3 is shown the percentage of adsorbed water lost at 150°C.; in the majority of the cases the percentages are high, a fact which we interpret as indicative of the

TABLE 5

The relation of planar water in soil colloids to base-exchange capacity (Ca-saturated colloids)

COLLOID	LABORATORY NUMBER	ADSORBED H_2O LOST AT 150°C.	BASE-EXCHANGE CAPACITY	H_2O LOST AT 150°C. (MOIST BASIS)	RATIO OF TOTAL WATER LOSS AT 150°C. TO BASE-EXCHANGE CAPACITY	MOLECULES H_2O PER EXCHANGE SPOT
1	*2*	*3*	*4*	*5*	*6*	*7*
		per cent	*m.e. per 100 gm.*	*gm. per 100 gm.*		
Cecil	11954	67.6	17	2.66	0.156	8.65
Sierra	16309	80.5	19	2.89	0.152	8.44
Redding	16318	84.7	35	5.38	0.154	8.55
Redding	16304	87.0	31	5.01	0.162	9.00
San Joaquin	6530	98.0	27	3.91	0.145	8.06
Placentia	7092	83.4	25	3.92	0.157	8.72
Yolo	7083	90.2	67	8.98	0.134	7.48
Yolo	17557	55.8	56	7.91	0.141	7.84
Susquehanna A	16312	59.4	30	4.73	0.158	8.78
Susquehanna B	16313	65.0	38	6.68	0.175	9.72
Susquehanna C	17554	78.2	60	7.84	0.131	7.28
Susquehanna D	17555	87.4	62	9.18	0.148	8.23
Susquehanna E	17556	92.0	95	14.18	0.149	8.28
Putnam	.....	67.6	60	....	.....	....

presence of planar water. Probably these colloids contain O^{--} or OH^{-} planes, and furthermore, these planes appear to be of greater extent than the broken-bond areas, from which one would conclude that the particles are of platy shape. This conclusion is supported by optical data.

In column 6 of table 5, the 150°C. water (absolute basis) has been divided by the base-exchange capacity; a surprisingly constant ratio results. As shown in column 7, from 7 to 9 water molecules are associated with each exchange spot, or 14 to 18 per adsorbed Ca ion. These values are much too high to be explained by Ca-ion hydration alone. Other attraction spots for water must exist on the clay surface, namely, the broken bonds and the planes.

In figure 20 the exchange capacities are plotted against the water loss at

150°C. Two curves result. First we have the minerals consisting exclusively of linked tetrahedra with broken-bond water. Quartz, felspars, and zeolites center around a common line. The second curve comprises the bentonite and soil colloids. It is much steeper than the lower curve because the number of water molecules per exchange spot is several times greater. The nearly linear relation in the case of the soil colloids strongly suggests that the soil-colloid surfaces are more like those of the bentonites and distinctly different from the

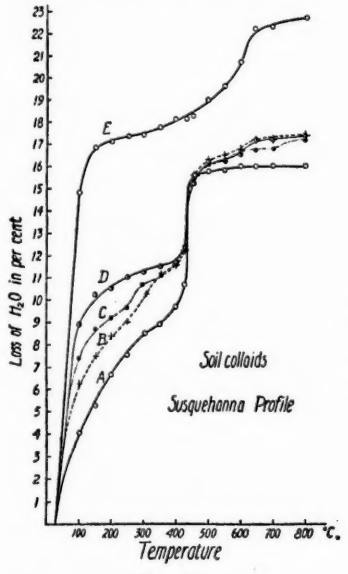

FIG. 19

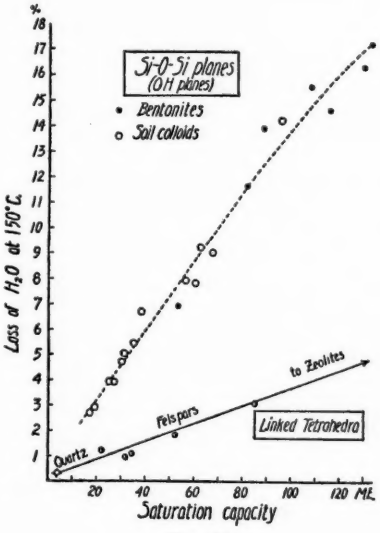

FIG. 20

FIG. 19. DEHYDRATION CURVES OF COLLOIDS EXTRACTED FROM THE SUSQUEHANNA PROFILE

Note the characteristic changes occurring with increasing depth (A → E). Curve E closely resembles that of Bentonite No. 7 (fig. 4).

FIG. 20. TOTAL WATER LOSS AT 150°C. AS A FUNCTION OF BASE-EXCHANGE CAPACITY

The soil colloids fall in line with the bentonitic colloids, which contain relatively much planar water, rather than with the felspar-zeolite minerals, which contain broken-bond types of water.

linked tetrahedra type. One is inclined to consider this as additional evidence of the existence of O^{--} and OH^{-} planes in soil colloids.

SUMMARY OF SOIL COLLOID STUDIES

The following conclusions appear to be justified: Soil colloids contain water of crystallization or, more precisely speaking, OH ions, as parts of a crystal lattice structure. This may be considered as an independent proof of the

crystalline nature of the colloidal particle (7). Unlike the minerals of known structure, the soil colloids lose their lattice water at lower temperatures. Whether this is caused merely by particle size or indicates a structural peculiarity, or both, must be further investigated. At least two major classes of soil colloids appear to exist: those which resemble in some measure kaolinite and halloysite; and those which appear to be related to (but not identical with) beidellite. In all cases, however, the composition of the surfaces seems to be rather similar; Si-O-Si planes and possible OH planes probably exist, and planar water dominates over broken-bond water.

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SOIL SWELLING: II. SWELLING OF SOIL IN SOLUTIONS OF ELECTROLYTES; MICROSCOPIC AND X-RAY INVESTIGATIONS

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Various theories exist concerning the influence of neutral salts on swelling. The old theory that cations and anions of salts exert a specific action on swelling is based on the ideas of Hofmeister, who established ion sequences and their rôle in this process.

Loeb objects to the ion sequences of Hofmeister. He assumes that cations and anions do not exercise any specific influence on the phenomenon of swelling and that the influence of salts is determined by the active acid reaction of the medium (pH). Chlorides, bromides, nitrates, and other anions in the form of neutral salts do not play any rôle.

On the contrary, new researches have demonstrated that the action of acids on the swelling of proteins depends not only on the pH but to a considerable degree on the nature of the anion also (17). This was demonstrated with still more conclusive evidence by Meunier and Rey (15), who confirmed the applicability of the anion sequences to the swelling of wool in neutral salt solutions though at the moment of equilibrium the pH varied within a wide range (from 4.5 to 7.4).

Michaelis (16) explains the action of very dilute solutions of salts by the size and kind of the charge of their ions. No specific difference is observed in the action of different ions. At high dilutions the action of ions may be explained by the concentration of H ions (pH). On the contrary, in concentrated solution the influence of the specific action of the salt ions takes the first place.

The influence of salts on the swelling of soil colloids and of bentonite has been studied by Mattson (3, 14). He has shown that in accordance with Donnan's equilibrium swelling decreases as a result of the addition of free electrolytes. The higher the valence of the ion of the same sign as the colloid's charge the less is this decrease of swelling. The higher the valence of the ion of the sign opposite to that of the colloid's charge the greater is the decrease of swelling. Hofmeister's sequences are applicable to soils also. The influence of the cations is, however, not quite clear here.

Herzog (6) in his investigation of the swelling of cellulose thinks it possible to apply to the explanation of the phenomena of swelling in electrolyte solutions the notions developed by Fajans in regard to the hydrophillic nature of ions. The sequence of ions according to their hydrophillic nature is represented by him as follows:

Monovalent cations—$H > Li > Na > K > Rb > Cs > NH_4$
Divalent cations—$Mg > Ca > S_2 > Ba$
Monovalent anions—$F > Cl > Br > J \sim NO_3 \sim ClO_3 \sim CNS > OH$
Divalent anions—$CO_3 > SO_4$.

The cations hydrate more strongly than the anions. Swelling decreases with the decrease of the hydrophillic nature of cations. The swelling capacity expresses the sum total of the hydrophillic nature of the ions composing the salt.

An almost similar sequence of cations according to their influence on hydration of clay is presented by Baver and Horner (1)

$$H > Mg > Ca > Li > Ba \gtrless Na > K.$$

EXPERIMENTAL

The experiments on swelling in solutions of electrolytes were designed to regulate the process of swelling in soil by means of adding salts, e.g., calcium salts; to study the influence of salts on structure stability; and to observe simultaneously swelling and absorption.

TABLE 9

Swelling of columnar alkali soil in $CaCl_2$ solutions

CONCENTRATION OF SOLUTION (AVERAGE)	Q	K_Δ	P_Δ	W_q	S	$\frac{K_\Delta}{P_\Delta}\cdot 100$	ABSORPTION PER 100 GM.
							m.e.
Water	21.66 ±0.69	40.05 ±0.7	46.44	13.16	0.58	86.22	0
0.1 *N*	25.38	41.58	47.84	12.81	0.59	86.9	4.71
1.0 *N*	21.25	39.17	49.40	12.63	0.59	79.46	39.80
4.0 *M*	11.25	29.76	43.55	8.42	0.68	68.33	.....

TABLE 10

Swelling of loamy chernozem in $CaCl_2$ solutions

CONCENTRATION OF SOLUTION (AVERAGE)	Q	K_Δ	P_Δ	W_q	S	$\frac{K_\Delta}{P_\Delta}\cdot 100$	ABSORPTION PER 100 GM.
							m.e.
Water	15.30 ±0.18	42.36 ±0.58	55.53	8.71	0.76	76.13	0
0.1 *N*	14.32	40.65	54.30	7.66	0.78	74.82	0
1.0 *N*	12.76	39.80	54.49	7.58	0.78	73.06	0
4.0 *M*	6.15	32.40	50.0	3.23	0.89	64.80	.....

The influence of the cations Ca, Mg, Na, Ba, and H was studied. For the sake of comparison all the salts were taken in the form of chlorides; the only acid employed in these tests was H_2SO_4. The fact that the curve of swelling may express either stabilization or the coagulation of the sol in respect to the electrolyte (18) was taken into account. The method used for studying swelling in the solutions of electrolytes was described in our preceding work[1] (20).

[1] The following values are the same as in the preceding work (20). Q = maximum swelling in volume units. K_Δ = the amount of solution absorbed in cc. P_Δ = the changed total porosity of the swollen soil. Wq = "swelling water" = "swelling solution." S = structure coefficient. $\frac{K_\Delta}{P_\Delta}$ = the capillary relative porosity.

TABLE 11

Swelling of columnar alkali soil in $MgCl_2$ solutions

CONCENTRATION OF SOLUTION (AVERAGE)	Q	K_Δ	P_Δ	W_q	S	$\frac{K_\Delta}{P_\Delta}\cdot 100$
Water	21.66 ±0.69	40.05 ±0.7	46.44	13.16	0.58	86.22
0.1 *N*	20.45	40.0	47.03	13.60	0.57	85.05
0.5 *N*	21.09	40.19	47.23	13.49	0.57	85.10
1.0 *N*	19.17	36.15	46.45	10.90	0.63	77.82

TABLE 12

Swelling of loamy chernozem in $MgCl_2$ solutions

CONCENTRATION OF SOLUTION (AVERAGE)	Q	K_Δ	P_Δ	W_q	S	$\frac{K_\Delta}{P_\Delta}\cdot 100$	ABSORPTION PER 100 GM.
							m.e.
Water	15.30 ±0.18	42.36 ±0.58	55.53	8.71	0.76	76.13	0
0.1 *N*	13.24	40.97	53.51	8.38	0.76	76.54	1.68
1.0 *N*	15.56	39.75	52.34	6.40	0.81	75.94	13.80

TABLE 13

Swelling of columnar alkali soil in $BaCl_2$ solutions

CONCENTRATION OF SOLUTION (AVERAGE)	Q	K_Δ	P_Δ	W_q	S	$\frac{K_\Delta}{P_\Delta}\cdot 100$
Water	21.66 ±0.69	40.05 ±0.7	46.44	13.16	0.58	86.22
0.1 *N*	20.13	38.76	45.09	12.74	0.59	85.97
1.0 *N*	17.71	37.15	47.43	12.35	0.60	78.33

TABLE 14

Swelling of columnar alkali soil in NaCl solutions

CONCENTRATION OF SOLUTION (AVERAGE)	Q	K_Δ	P_Δ	W_q	S	$\frac{K_\Delta}{P_\Delta}\cdot 100$
Water	21.66 ±0.69	40.05 ±0.7	46.44	13.16	0.58	86.22
0.1 *N*	19.57	39.93	45.85	13.90	0.57	87.09
0.5 *N*	19.25	38.97	45.45	13.19	0.58	85.74
1.0 *N*	21.89	36.53	44.36	11.39	0.62	82.35

Tables 9–17 show the results of these experiments. In computing the value of K_Δ the amount of solution absorbed was expressed in cubic centimeters, its specific volume being taken into account. This makes the values of K_Δ comparable. As an indicator of swelling we use the quantity we call "swelling

TABLE 15

Swelling of columnar alkali soil in H_2SO_4 solutions

CONCENTRATION OF SOLUTION (AVERAGE)	Q	K_Δ	P_Δ	W_q	S	$\frac{K_\Delta}{P_\Delta}\cdot 100$
Water	21.66 ±0.69	40.05 ±0.7	46.44	13.16	0.58	86.22
0.1 *N*	20.44	38.46	47.82	12.38	0.59	80.42
0.5 *N*	25.24	37.39	50.59	9.73	0.65	73.91

TABLE 16

Swelling of loamy chernozem in H_2SO_4 solutions

CONCENTRATION OF SOLUTION (AVERAGE)	Q	K_Δ	P_Δ	W_q	S	$\frac{K_\Delta}{P_\Delta}\cdot 100$	ABSORPTION PER 100 GM.
							m.e.
Water	15.30 ±0.18	42.36 ±0.58	55.53	8.71	0.76	76.13	0
0.1 *N*	14.48	42.04	54.29	8.79	0.75	77.43	6.86
0.5 *N*	19.06	44.30	56.25	8.69	0.76	78.75	14.12

TABLE 17

Swelling of loamy chernozem saturated with Na to the amount of 27.94 per cent of its exchange capacity

CONCENTRATION OF SOLUTION (AVERAGE)	Q	K_Δ	P_Δ	W_q	S	$\frac{K_\Delta}{P_\Delta}\cdot 100$	ABSORPTION PER 100 GM.
							m.e.
Water	17.68	41.58	55.86	9.48	0.74	74.43	0
0.1 *N* $CaCl_2$	18.10	35.41	51.95	2.42	0.90	68.16	2.29
1.0 *N* $CaCl_2$	14.90	33.84	50.39	1.91	0.93	67.15	28.12

solution" (Wq), analogous to the "swelling water" of our preceding work, instead of the habitually used "volume increase."

The results of the determinations are shown in figures 2 and 3.

With loamy chernozem no absorption of Ca from the 0.1 *N* and 1.0 *N* solutions of $CaCl_2$ was observed. The swelling curves (Wq) for the two soils have one maximum for distilled water, from which they sink steadily parallel to the rise in the concentration of the solution. The curve of relative capillarity

$\left(\frac{K_\Delta}{P_\Delta}\right)$, which may be regarded as the curve of absorption of the solution, has the same trend as the curve of swelling with the difference that the former sinks more abruptly at high concentrations. The curve of absorption goes in the opposite direction (columnar alkali soil). With the increase in absorption of Ca, swelling decreases; therefore, the curve of absorption may be regarded as the curve of coagulation, the rise in which corresponds to the increase in the value of S, the index of "structure stability."

In the columnar alkali soil the absorption of $Mg^{\cdot\cdot}$ was not determined. The swelling curves (Wq) of columnar alkali soil and of loamy chernozem differ in

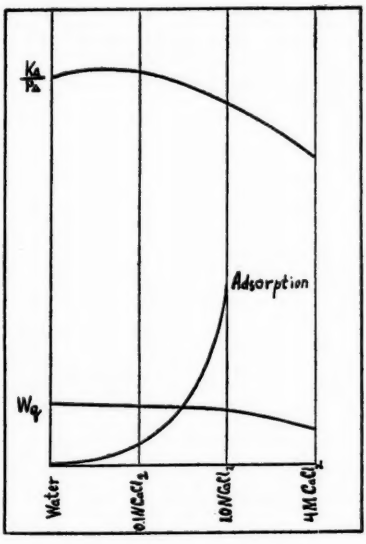

FIG. 2

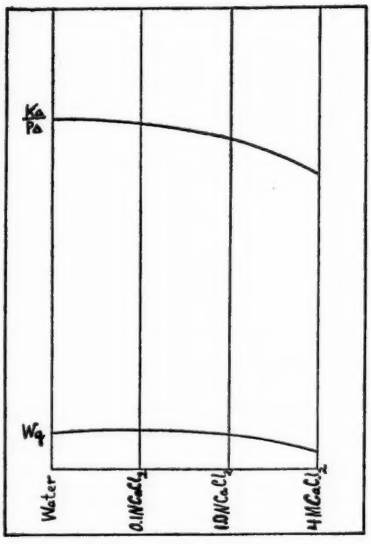

FIG. 3

FIG. 2. SWELLING OF COLUMNAR ALKALI SOIL IN $CaCl_2$

FIG. 3. SWELLING OF LOAMY CHERNOZEM IN $CaCl_2$

their trend. Whereas the chernozem curve descends noticeably from its maximum, which corresponds to distilled water, with the increase in concentration of the solution, that of the alkali soil has its maximum at 0.1 N, then descends gradually, its Wq value at 0.5 N concentration still remaining higher than that corresponding to water. For chernozem the curves of relative capillarity, $\frac{K_\Delta}{P_\Delta}$, have the same trend as has Wq; for alkali soil, a slightly different one. The curve of adsorption (coagulation) of $Mg^{\cdot\cdot}$ has, for chernozem, an opposite trend (fig. 4 and 5).

Swelling in $BaCl_2$ solutions is marked, as in $CaCl_2$ solutions, by the gradual

descent of its Wq curve and the more abrupt descent of its relative capillarity curve, $\frac{K_\Delta}{P_\Delta}$. Thus, the $BaCl_2$ graph resembles that of $CaCl_2$.

Swelling in NaCl solution produces an original curve, resembling the $MgCl_2$ one. As with $MgCl_2$ it reaches its maximum at 0.1 N concentration, and in 0.5 N solutions the value of Wq is higher than in water. The curve of absorption, $\frac{K_\Delta}{P_\Delta}$, has approximately the same trend as that of Wq (fig. 6 and 7). The S index remains almost stable.

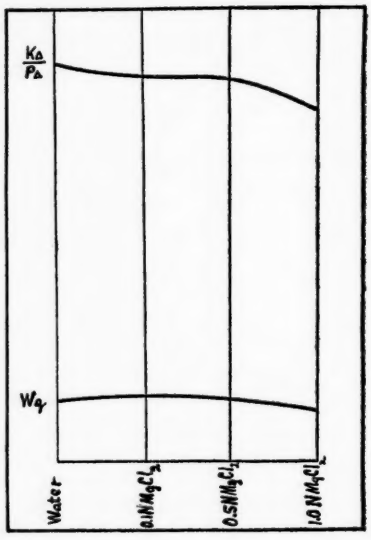

FIG. 4

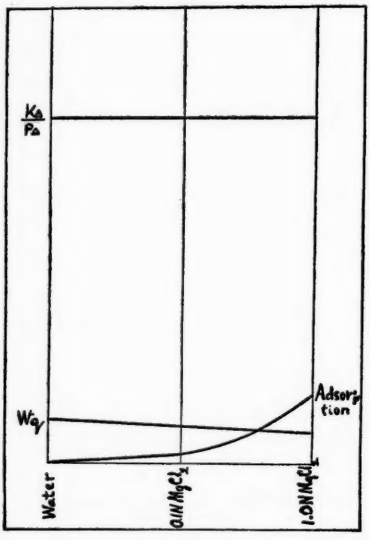

FIG. 5

FIG. 4. SWELLING OF COLUMNAR ALKALI SOIL IN $MgCl_2$
FIG. 5. SWELLING OF LOAMY CHERNOZEM IN $MgCl_2$

The swelling of columnar alkali soil in H_2SO_4 decreases with the increase in acid concentration. The trend of the curves of swelling (Wq) and of relative capillarity, $\frac{K_\Delta}{P_\Delta}$, is similar, as in those obtained for $CaCl_2$ solutions.

For chernozem the trend of the swelling and water absorption curves $\frac{K_\Delta}{P_\Delta}$ is opposite. With the increase in the absorption of acid we observe an increase in the absorption of water; this is not the case for columnar alkali soil. Apparently this increase in water absorption should be ascribed to the formation of a chemical compound with the acid or to the dissolution of the acid in soil and the formation of a solvate film (fig. 8 and 9).

The concluding experiment was conducted in $CaCl_2$ solutions with the swelling of loamy chernozem, in which part of the replaceable Ca was replaced

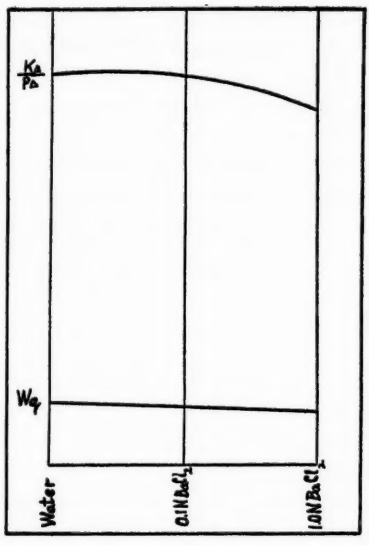

FIG. 6

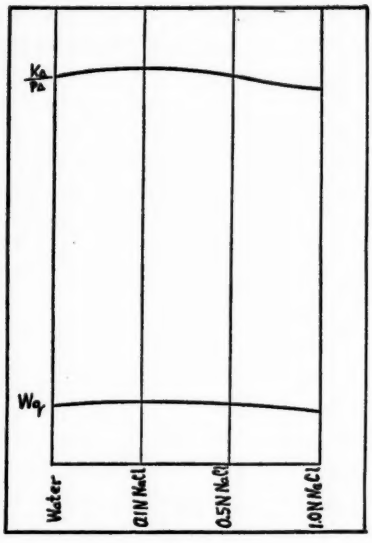

FIG. 7

FIG. 6. SWELLING OF COLUMNAR ALKALI SOIL IN $BaCl_2$

FIG. 7. SWELLING OF COLUMNAR ALKALI SOIL IN NaCl

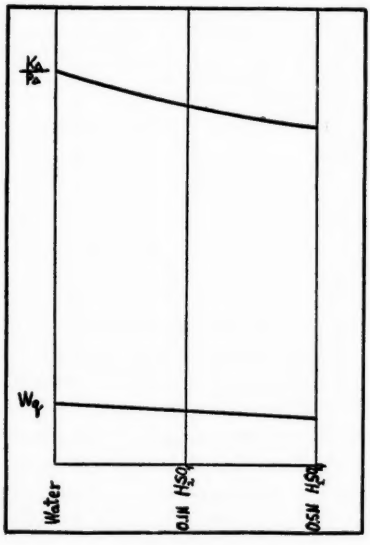

FIG. 8

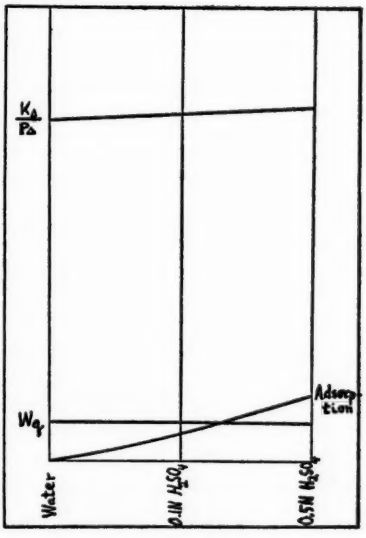

FIG. 9

FIG. 8. SWELLING OF COLUMNAR ALKALI SOIL IN H_2SO_4

FIG. 9. SWELLING OF LOAMY CHERNOZEM IN H_2SO_4

by Na to the amount of 27.94 per cent of the cation exchange capacity. Simultaneously absorption of $Ca^{\cdot\cdot}$ from 0.1 *N* and 1.0 *N* solutions of $CaCl_2$ was studied.

A similar, though less sharp picture, than that for columnar alkali soil in $CaCl_2$ solutions, was observed.

The trend of the swelling (Wq) curves and of those of water absorption is here the same, the difference being that here the decrease of swelling *reveals itself in a sharper form.* As the absorption of Ca increased from 2.29 m.e. to 28.12 m.e. the swelling fell from $Wq = 9.48$ to $Wq = 2.42$ and 1.91 (table 16). The value of the "structure stability" index S rose correspondingly (fig. 10).

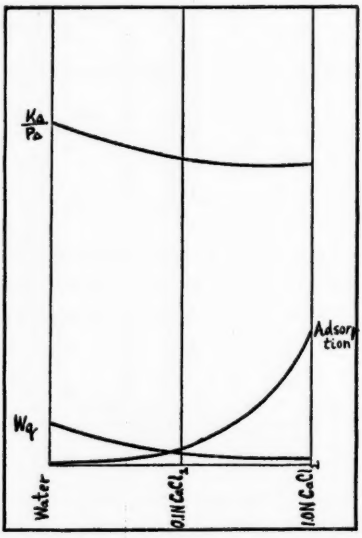

FIG. 10. SWELLING OF LOAMY CHERNOZEM SATURATED WITH $CaCl_2$ SOLUTION WITH Ca REPLACED BY Na TO AMOUNT OF 27.94 PER CENT

The experiments with swelling in various salt solutions confirm the theory that swelling is lowered by the presence of free electrolytes and that this phenomenon may be explained with the help of the osmotic theory of swelling. The lowering of swelling is directly connected with the absorption of cations. The minimum swelling is observed at the point at which this absorption reaches its maximum. Thus in determining the swelling the curve of absorption may be considered as representing the curve of the coagulation of the colloid solution. The increase of swelling in 0.1 *N* and 0.5 *N* solutions of $MgCl_2$ and NaCl as compared with swelling in distilled water may be explained by the fact that in the absorption of Mg and Na cations the electrolytic dissociation at first increases in comparison to that which took place during swelling in water and

later, after further addition of salt, it decreases. The action of acid solutions may also be explained from this point of view.

We must note further that hydration $\left(\frac{K_\Delta}{P_\Delta}\right)$ under the influence of the Ca ion in low concentrations of $CaCl_2$, for instance in solutions weaker than 0.1 N, is greater than in water or in similar solutions of $MgCl_2$, NaCl, and $BaCl_2$. This hydrating effect of calcium was indicated by Freundlich and Sachs for kaolin (4). Thus, in regard to hydration the position of Mg does not fully correspond to Baver's scheme.

Absorption of Ca has a marked effect on the lowering of swelling (Wq) only in the case of soils containing replaceable Na, e.g., columnar alkali soil, or the "artificial alkali soil" prepared from chernozem by saturating it with Na up to 27 per cent of its exchange capacity. Very characteristic of these soils is the "improvement" of their structure under the influence of free Ca ions. But this "improvement" is not the same in all soils investigated. It is less marked for columnar alkali soil than for Na-chernozem. The "structure index" rises from 0.74 (water) to 0.93 (1.0 N solution of $CaCl_2$). This "improvement," however, takes place only under the influence of strong solutions considerably exceeding the threshold of coagulation.

In soils saturated with calcium (for instance, in loamy chernozem,[2] which is practically 98 per cent saturated) swelling in $CaCl_2$ solutions proceeds almost identically with swelling in water, without any noticeable "improvement" of structure. Only in concentrated solutions (4 M) is a depression observed. The transformation of structural aggregates of such soils into water-tight ones by the addition of calcium salts apparently cannot be achieved. As microscopic investigation has shown, disintegration of the aggregates is very slight in concentrated solutions of $CaCl_2$.

A certain interest is aroused by the experiments on absorption by structureless non-swelling soils of the solutions of Ca and Mg salts and of H_2SO_4 and Na_2CO_3, in which cation absorption was studied. Omitting the description of these experiments we shall note only that salts have no effect on the absorption of their solutions in this case; its value remains always equal to that of the absorption of inert liquids. This circumstance is in accordance with the idea, already developed, that in structureless soil absorption of water or of solutions is essentially a purely capillary process.

MICROSCOPIC RESEARCH

Rather important results have been obtained in the study of swelling by applying microscopic and cinematographic technique. A number of remarkable researches may be cited, in which the understanding of the phenomena taking place in swelling was founded on microscopic investigation of the process. Most of these works concern the swelling of vegetable fibers and of silk: such works as the investigations by Weimarn (21) of the swelling of silk; by Hess, Trogus, et al. (8), of ramie fiber swelling; by Rabinowitch (19) and

[2] The replaceable cations of loamy chernozem are Ca, 46.3 m.e., and Mg, 0.03 m.e.

by Hess and Rabinowitch (7) on cellulose fibers; by Beiser (2) on the swelling of fir-tree and beech fibers.

In the present investigation an attempt was made to apply the microscopic methods to the study of soil swelling. The tests were made in passing light. The objects of observation were microstructural elements <0.25 mm. and <0.5 mm. in size. For the sake of comparison these microaggregates were studied under the microscope both in water and in oil, magnified 50–100 times. The photographs were taken at a magnification of about 70 times.

To eliminate the possibility of compressing air (13) into the aggregates and of their bursting, they were placed into a very thin layer of water deposited on an object slide.

The phenomena of the desintegration of the aggregates, foretold on the basis of the comparative study of water and oil absorption, can be clearly seen under such conditions of the experiment. Under the microscope one may see how water penetrates into the minuscule cracks, <0.01 mm., that arise during swelling and divides the microaggregates into still lesser units.

In oil the character of the phenomena observed is quite different. Here no disintegration of the aggregates or penetration of oil into the micropores is observed. The aggregates act as indivisible elements.

The photographs, taken at the same magnification, represent the microaggregates of columnar alkali soil: plate 1, figure 1, in oil, and figure 2, in water; and those of loamy chernozem: plate 1, figure 3, in oil, and figure 4, in water.

The size of the aggregates was accidentally different, but this does not disguise the different character of the absorption of oil and of water, so characteristic of structural soils as has been indicated.

In structureless soils other relations were observed. Experiments had shown that in such soils there was no difference between the absorption of oil and that of water. Therefore one could expect that under the microscope there would be no difference either. Indeed, as may be seen from plate 1, figures 5 and 6, representing the absorption of oil and that of water by loess-like loam, there is a similarity of action, consisting in the almost complete subdivision of the soil into mechanical elements. If "clods" are observed, they do not produce that characteristic picture of disintegration which is observed in structural soils. There is no splitting of aggregates (pl. 1, fig. 6), because there are no aggregates here.

As still greater evidence to prove this, we reproduce a photo showing particles of loess-like loam in a saturated solution of $CaCl_2$ (pl. 1, fig. 7). As was demonstrated earlier in the chapter on swelling in solutions of electrolytes, saturated solutions of $CaCl_2$ produce a considerable lowering of swelling. This was confirmed for structural soils by microscopic tests. The aggregates of such soils (see hereinafter) do not split at all or show but slight disintegration when placed in a saturated solution of $CaCl_2$. One would expect, therefore, that in a saturated solution of $CaCl_2$ the aggregates of loess-like loam, if they

exist, must remain intact. Figure 7, plate 1, however, shows a picture identical to that of figure 6, as if the loess-like loam in it was not in $CaCl_2$ but in water.

Thus microscopic investigation confirms the conclusion, arrived at earlier, that absorption of polar and non-polar liquids permits sharp distinction between structural and structureless soil and that water absorption by structural soil is closely connected with an unsettling of this structure and an increase in the degree of dispersion of this soil.

Simultaneously with the study of water absorption, microscopic investigation of the influence of solutions of electrolytes on the aggregates of structural soils was conducted.

As can be seen from the foregoing discussion, the action of salt solutions lowers the swelling. This lowering proved, however, to be rather small, as compared with swelling in water, even for 1.0 *N* solutions. Only in the case of the saturated solution of $CaCl_2$ were a considerable lowering of swelling and an almost complete "restoration" of structure noted. Microscopic investigation confirms these results. Figures 1 and 2, plate 2, represent the swelling of columnar alkali soil aggregates in 1.0 *N* and in saturated solutions of $CaCl_2$.

Figures 3, 4, and 5, plate 2, represent the swelling of loamy chernozem in 0.1 *N*, 1.0 *N*, and saturated solutions of $CaCl_2$. It may be observed in them that the disintegration of alkali soil aggregates in 1.0 *N* solutions of $CaCl_2$ is somewhat less than in water (pl. 1, fig. 2).

The same thing may be observed for loamy chernozem also (fig. 3 and 4, plate 2). In saturated solutions of $CaCl_2$ the aggregates of both the columnar alkali soil and the chernozem (fig. 2 and 5, plate 2) show considerably less splitting than in 1.0 *N* solution of $CaCl_2$. This is in good agreement with the values we found for the "swelling solution" (*Wq*).

Figures 6 and 7, plate 2, represent respectively the swelling of columnar alkali soil and loamy chernozem in a normal solution of $MgCl_2$. Here, in contradistinction to $CaCl_2$, hydration (disintegration) is, as has already been noted, less in the same degree in both alkali (fig. 6, pl. 2) and chernozem (fig. 7, pl. 2) soils. The latter circumstance agrees with the results obtained for $MgCl_2$ in the swelling experiments.

Figures 1 and 2, plate 3, represent the swelling of columnar alkali soil and loamy chernozem in 0.5 *N* solution of H_2SO_4. The disintegration of the chernozem aggregates (fig. 2, pl. 3) is almost the same as in water; that of the alkali soil aggregates (fig. 1, pl. 3) is somewhat less. This also is in agreement with the results of the experiments.

X-RAY INVESTIGATION

It was noted at the beginning of this article that the application of X-ray analysis to the study of swelling has acquired the importance of a method, revealing the essence of structural changes in almost every case in which the swelling substance is composed of the crystalline phase. The most detailed research work of this kind was done by Katz and Mark (11) on cellulose, by

Hofmann and Endell (9) on the swelling of the argillaceous mineral montmorillonite, and by Hofmann and Frenzel (10) on the swelling of graphitic acid.

The purpose of the present investigation was to elucidate the character of the structural changes in the soil during swelling. The supposition that soil suspensions consist of crystalline substance was based on the works of Hendricks and Fry (5) and of Kelley, Dore, and Brown (12).

The first roentgenoscopic determinations[3] concerned a sample of columnar alkali soil the components of which were kept undivided. The roentgenograms were obtained by the Debay method in chromium rays with a wavelength of $K_\alpha = 2.287$ Å and $K_\beta = 2.08$ Å, in a chamber 57.4 mm. in diameter.

To protect the swollen soil sample from evaporation during the roentgenographic operation, which lasted 9 hours, it was put into a thick celluloid tube. The soil did not dry out in such a tube during 48 hours. The lines obtained in the roentgenograms (fig. 3 and 4, pl. 3), with the possible exception of one, coincide with the lines of crystalline quartz.

No difference can be observed between dry and swollen soil in these roentgenograms. This led us to suppose that, besides quartz, there may be other minerals in soil capable of taking part in swelling but that they are found in soil in such small quantities, as compared with quartz, that they cannot produce the corresponding interferences in the roentgenogram.

To verify this, a suspension was isolated from columnar alkali soil, consisting of particles smaller, and for the most part much smaller, than 1 μ. In investigating these suspensions—both dry and swollen—(figs. 5, 6, 7, and 8, pl. 3) either no lines were found or there appeared a system of weak lines of crystalline quartz. Besides these, two weak lines are observed in both the dry and the swollen suspensions. Besides the suspension of columnar alkali soil, another suspension isolated from loess-like loam was also tested roentgenographically. This suspension, like that of columnar alkali soil, produced identical roentgenograms in dry and swollen condition. A similar roentgenogram was produced by the suspension of columnar alkali soil swollen in 1.0 N solution of $CaCl_2$ (fig. 9).

The results show that suspensions of columnar alkali soil and of loess-like loam contain an insignificant quantity of crystalline quartz and some other mineral, the nature of which we were not able to determine by the two weak lines it produced. It should be noted that these lines do not coincide with those of montmorillonite, bentonite, and galloisite, i.e., of typical mineral soil colloids.

Thus in the samples tested crystalline substance does not take any part in the swelling process. The main mass of the suspension of columnar alkali

[3] The roentgenoscopic study of swelling was conducted in the Institute for Fireproof Materials, Kharkov, under the supervision of the chief of the X-ray laboratory of this institute, B. J. Pines, to whom I consider it my duty to express my thankfulness for valuable aid and suggestions.

soil consists of amorphous substance, which is responsible for the changes connected with soil swelling.

SUMMARY

The influence of solutions of electrolytes on swelling was studied. It was found that solutions of salt and of H_2SO_4 lower swelling, with the exception of 0.1 *N* and 0.5 *N* solutions of NaCl and $MgCl_2$.

Parallel with the study of the swelling of soil in solutions of electrolytes, a study was made of the absorption of cations. It was found that the curve of absorption has an opposite trend to the curve of swelling. The curve of absorption may be regarded as the curve of the coagulation of the sol of the soil colloid.

Microscopic investigation confirmed the method by which a sharp difference between structural and structureless soil was established on the basis of absorption of water and of inert liquids by soil.

Microscopic investigation of swelling in solutions of electrolytes gives results coinciding with the values found for "swelling solution." This confirms the correctness of the choice of "swelling water" ("swelling solution") as an indicator determining the process of swelling in its proper quality.

Roentgenographic investigation of suspensions isolated from structural and structureless soils showed that they contain but slight amounts of crystalline substance, the prevalent mineral of which is quartz. It is demonstrated that crystalline substance takes no part in the process of swelling. The main mass of the suspension of columnar alkali soil consists of amorphous substance with which the process of change is closely connected.

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PLATE 1

FIG. 1. Columnar alkali soil in oil.
FIG. 2. Columnar alkali soil in water.
FIG. 3. Loamy chernozem in oil.
FIG. 4. Loamy chernozem in water.
FIG. 5. Loess-like loam in oil.
FIG. 6. Loess-like loam in water.
FIG. 7. Loess-like loam in saturated $CaCl_2$.

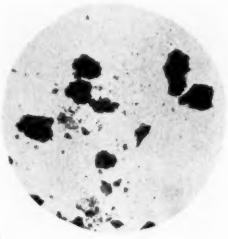
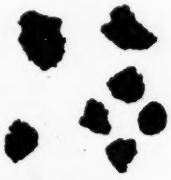


FIG. 1

FIG. 2



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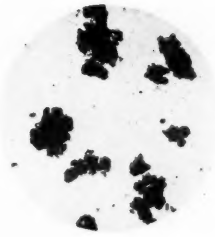

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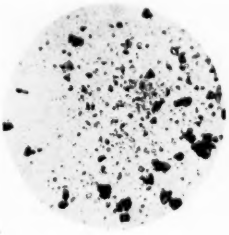

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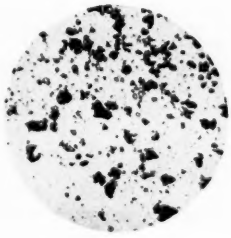


FIG. 6

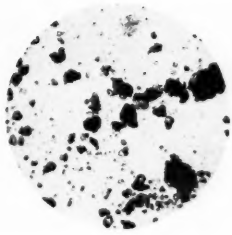
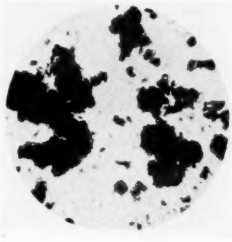


FIG. 7

PLATE 2

FIG. 1. Columnar alkali soil in 1.0 N $CaCl_2$.
FIG. 2. Columnar alkali soil in saturated $CaCl_2$.
FIG. 3. Loamy chernozem in 0.1 N $CaCl_2$.
FIG. 4. Loamy chernozem in 1.0 N $CaCl_2$.
FIG. 5. Loamy chernozem in saturated $CaCl_2$.
FIG. 6. Columnar alkali soil in 1.0 N $MgCl_2$.
FIG. 7. Loamy chernozem in 1.0 N $MgCl_2$.



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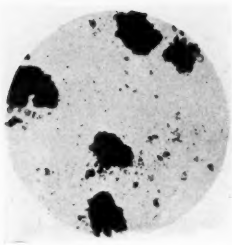
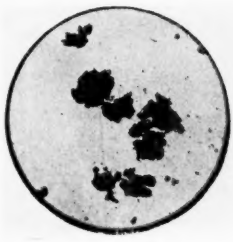


FIG. 2



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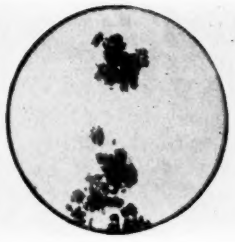


FIG. 4

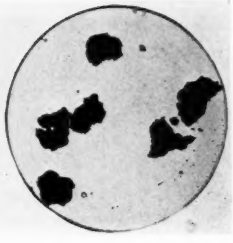


FIG. 5

FIG. 6

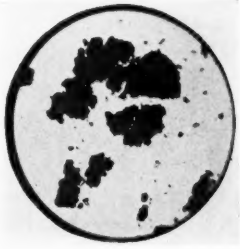


FIG. 7

PLATE 3

FIG. 1. Columnar alkali soil in 0.5 N H_2SO_4.
FIG. 2. Loamy chernozem in 0.5 N H_2SO_4.
FIGS. 3–9. Roentgenograms of dry and swollen columnar alkali soils.

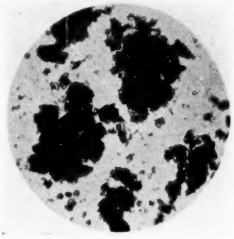


FIG. 1

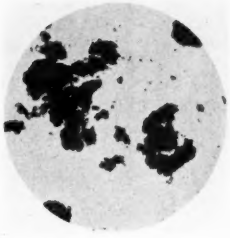


FIG. 2

FIG. 3

FIG. 4

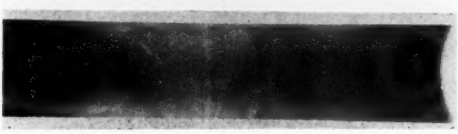
FIG. 5

FIG. 6

FIG. 7

FIG. 8

FIG. 9



STUDIES ON PODZOLS AND BROWN FOREST SOILS: II

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In the first part of this paper it was demonstrated that podzols and brown forest soils differ not only in their morphological but also in their chemical nature (3). Tamm's acid-oxalate method proved to be very useful for the study of those differences, but there are several other ways of demonstrating them. Some of the ways of showing evidences of podzolization have been discussed by Joffe (1), and Mattson has recently pointed out that "the most rational method is to be found in a determination of the amphoteric points of the respective complexes" of the different horizons in the soil profile (13, p. 472). The conception of the soil colloids as ampholytoids (10) led to the theory of isoelectric weathering (11), according to which the composition and the properties of the colloids depend on the type of weathering prevailing in the soil.

In the case of the podzols the weathering can be considered as a typical acid hydrolysis. The colloidal residue in the upper, acidic horizons (A) of a podzol profile is strongly acidoid, whereas the basoids (or rather ampholytoids), being ionized, move farther down with the percolating water. In the B horizons where the sol encounters a higher prevailing pH it is precipitated, and the gel formed has a less acidoid (more basoid) character than the colloids left in A. The opposite type of weathering, a basic hydrolysis, is represented by the laterites. Here the pH in the upper part of the profile is high enough to prevent the ionization and dispersion of the ampholytoids, whereas the acidoids move downward, leaving a residue high in sesquioxides. In the case of the brown forest soils it has been demonstrated that the colloids, especially the sesquioxides, as determined by the acid-oxalate method, are evenly distributed in the A and B horizons of the profile or have their maximum in A (2, 3). This would indicate, from the standpoint of isoelectric weathering, that these soils are formed under circumstances causing a weathering of less acid type than the podzols where the sesquioxides are removed from the colloid complex of the A horizons.

In the following pages are given the results of a study of the amphoteric

[1] The laboratory work involved in this study was done by the author in the laboratory of Dr. Sante Mattson during a stay as Cook-Voorhees Research Fellow at the New Jersey Agricultural Experiment Station October, 1931–September, 1932 [see acknowledgment in the first part of this paper (3)].

reactions of the soil from the various horizons of podzol and brown forest soil profiles. The profiles are the same as those used in the first part of this paper (3, p. 146–148), that is, profile 1 is the typical brown forest soil from Hissö, province Småland, Sweden; profile 2 is a podzol from the same province; profile 3 is an aclimatic brown forest soil from Siljansfors, province Dalarna, Sweden; profiles 4, 5, and 6 are typical iron podzols from different plant communities at Siljansfors; and profile 7, from the same place, is a podzol related to the iron humus podzol of Tamm (14, p. 366).

IONIC EXCHANGE

The ion exchange capacity, that of both the cation and the anion, is a most significant expression of the nature of colloidal complexes. It has been demonstrated that the cation exchange capacities at pH 7 increase with the proportion of acidoid to ampholytoid in the complex and also that in the same type of complexes the exchange capacity is higher the weaker the basic properties of the ampholytoid present (9). This is exactly what the theory of the amphoteric nature of colloids requires and must be true at any given pH down to the point of exchange neutrality. For the anion exchange capacity the rule must be the opposite: it decreases with an increasing acidoid ampholytoid ratio.

Let us now see how the ion exchange capacities should vary in the different layers of soils.

Take first the cation exchange capacity. If the theory of isoelectric weathering be true the base exchange per gram colloid should be higher in a podzol than in a soil formed by a less acid type of weathering. And in a podzol there should be a higher base exchange in the A horizons than in the B because the ampholytoids, such as the sesquioxides, are leached out from A and redeposited in B, thus making the colloids there less acidoid. But now we must remember that the ion exchange capacity, determined on the whole soil, is not only a qualitative but also a quantitative property. It is well known—and was proved in the first part of this paper—that the colloids are generally far more abundant in B than in A. Despite the fact that the mineral *colloid complex* in the A horizons of a podzol profile has a much higher base exchange capacity than the one in B it can therefore very well happen that *the whole soil* has a lower base exchange in A than in B. If this be the case, and as will be shown later it is generally true for the A_2 horizons, it is a proof of the poverty of colloids in these horizons. From this discussion it is clear that the base exchange capacity, because of its qualitative and quantitative nature, cannot be used as a means of characterizing the type of soil formation unless some other determinations are made to show the acidoid/ampholytoid ratio of the complexes.

What will be the result of determinations of the anion exchange capacities? Here we must find that the more the ampholytoid prevails in the complex and the more basic its character, the higher is the anion exchange capacity.

TABLE 6

Isoelectric point, exchange neutrality, ultimate pH, base exchange, combining capacity at pH 7, base saturation, and actual pH of samples from the different horizons of podzols and brown forest soils

PROFILE NUMBER	SOIL TYPE	HORIZON	ISOELECTRIC POINT	ULTIMATE pH	pH OF EXCHANGE NEUTRALITY	BASE EXCHANGE, M.E. PER 100 GM.	COMBINING CAPACITY AT pH 7, M.E. PER 100 GM.	BASE SATURATION AT THE pH OF THE NATURAL SOIL, PER CENT	pH OF THE NATURAL SOIL	ELECTRODIALYZABLE BASES, M.E. PER 100 GM.
1	Brown forest soil, typical	A	...	4.1	4.0	25.93	11.5	63	6.1	4.47
		B_1	...	4.8	4.4	12.85	10.5	26	5.7	0.74
		B_2	3.7	5.4	5.1	9.18	5.7	31	5.9	0.42
		C_1	3.9	5.4	5.5	4.33	1.5	50	6.1	0.34
		C_2	3.9	5.4	5.3	7.19	2.2	45	5.9	0.24
2	Podzol	A_2	...	4.0	4.0	19.20	7.5	−7	4.0	0.15
		B_1	4.0	5.4	5.3	18.17	13.0	−19	4.7	0.09
		B_2	4.0	5.4	5.7	10.11	4.8	−94	4.9	0.51
		C_1	5.1	5.4	6.0	15.20	2.0	−75	5.3	0.19
		C_2	5.2	5.5	6.3	2.18	0.2	−50	6.2	0.07
3	Brown forest soil, acli-matic	A	...	4.3	4.1	107.00	circ. 60.0	circ. 50	4.8	28.40
		B_1	...	4.6	4.8	10.34	7.5	57	6.1	0.49
		B_2	...	4.5	5.0	3.93	2.5	70	6.2	0.55
		B_3	...	4.5	4.8	6.91	3.9	77	6.2	0.22
4	Iron podzol	A_2	...	3.9	3.9	4.29	3.0	−17	4.1	0.08
		B_1	4.1	5.7	5.6	9.36	3.5	36	6.1	0.10
		B_2	4.1	5.8	5.7	4.51	2.3	22	6.1	0.71
5	Iron podzol	A_2	...	4.2	4.1	3.23	5.0	5	4.5	0.94
		B_1	4.2	5.1	5.0	11.14	20.0	13	5.8	0.95
		B_2	4.3	5.6	5.4	2.97	2.3	33	6.1	0.91
		C_1	4.8	4.6	5.3	1.32	1.0	50	6.2	0.86
		C_2	4.7	4.5	5.3	1.39	1.0	50	6.2	0.59
		C_3	...	4.5	5.3	1.63	1.0	50	6.2	0.67
6	Iron podzol	A_0	...	3.5	3.0	114.88	20.0	....	3.8	10.55
		A_2	...	4.1	4.0	6.54	4.5	0	4.1	0.52
		B	5.3	5.7	6.0	7.52	3.2	8	6.1	0.26
		C	5.0	5.9	6.5	1.10	0.2	−50	5.9	0.17
7	Iron humus podzol	A_2	...	4.2	4.1	5.87	3.5	23	4.7	0.42
		B_1	3.7	5.4	4.6	38.63	25.0	20	5.7	0.30
		B_2	3.8	4.9	4.8	28.92	29.0	23	5.7	0.28
		C	3.4	4.7	5.3	2.37	2.7	28	5.9	0.35

In a podzol profile we should therefore expect to find a higher exchange capacity in the B horizons, with their accumulation of sesquioxides and other ampholytoids, than in the A horizons. In the case of a very marked basic type of weathering we could perhaps have somewhat the same difficulty in interpreting the results as in the case of the base exchange in the podzols. But generally the anion exchange capacities of the different horizons would well characterize the type of soil formation. In any case a combination of determinations both of the anion and the cation exchange capacities would give good information of the soil type and the nature of the colloids and, to a certain extent, even give a relative measure of the amounts of colloids present.

Determinations of the base exchange were made in the following way. Five grams of air-dry soil, passed through a 2-mm. sieve, was put in a beaker, some neutral *N* barium acetate solution was added, and the contents were gently stirred. After some time the liquid and the soil were transferred to a filter and then the soil was leached with small portions of the barium acetate solution until the filtrate showed neutral[2] reaction (in all cases brom thymol blue was used as an indicator), and then a few times more. A total volume of 250 cc. was always used. The filter was then filled with neutral *N* barium chloride solution (10 cc.), and, when this had passed through, the residue was washed with cold distilled water until the filtrates showed no chloride reaction. All "exchangeable bases" are then supposed to be displaced by barium and all "free" barium salts removed by washing. The residue on the filter was then treated with small portions of *N* ammonium chloride solution at a temperature of 70°C. In all, 250 cc. of this solution was used for each sample. The barium was determined as $BaSO_4$ in the common way. The results, are shown in table 6 where the Ba displaced by NH_4, the base exchange capacity, is given in milliequivalents per 100 gm. of oven-dry soil (105°C.). They will be discussed later in connection with the points of exchange neutrality and will here merely be summarized as follows. The base exchange of the brown forest soils decreases from the A to the B and C horizons. In the podzols two clear maxima of base exchange occur, one in A_0, because of its high humus content, and one, though much smaller, in the upper part of B; this depends on the higher amount of colloids in B as compared to A_2 and C, where the actual colloids present must have the highest exchange capacity in the A horizon. The results obtained from the different iron podzols seem to confirm the previously expressed idea that the acid-oxalate method gives a measure of the reactive colloids. At least the differences in exchange capacity can be explained from the composition of the colloids thus determined.

[2] Whether the determinations be made at pH 7 or at any other pH above the point of exchange neutrality is naturally entirely arbitrary, provided all determinations be made at the same pH; there will always be a difference between the soils depending on the composition and the amounts of colloids present. But a linear relationship between base exchanges determined at different pH values can not be expected because of the possible differences in the linkage within the micellae of the colloid complex at different reactions.

CATAPHORESIS

The isoelectric point has been found to vary with the composition of the soil colloidal complex in such a way that this point lies at a higher pH the higher the basoid (sesquioxide) constituents of the complex, whereas a complex having a high acidoid (silica, humus) content is isoelectric at a low pH. Since the isoelectric complex represents its most stable condition we should, according to the theory of isoelectric weathering, under conditions of a heavy leaching and a high maturity, expect to find the composition and therefore also the isoelectric point of the soil colloid corresponding to the prevailing pH of the soil. In the case of many of the natural soils the isoelectric weathering is more of a tendency to an ultimate condition than a fully established fact. We must remember that colloids flocculate not only at the isoelectric point but also in a more or less wide range of pH in the neighborhood of this point (7). In any case the isoelectric point indicates the nature of the colloids in the soil and should give information about the type of weathering prevailing.

The isoelectric point was determined by cataphoresis measurements, using the apparatus described by Mattson (6). The air-dry soil samples (5 gm. of each) were shaken in rubber stoppered test tubes with 0.01 *N* NaCl solution containing different amounts of HCl. The reason for using NaCl solution instead of pure water for the suspension is that the salt so hastens the attainment of equilibrium that the measurements can be made the day after mixing (13, p. 472). After repeated shaking the test tubes were left undisturbed for a day. Then small samples of the clear solutions were taken for colorimetric pH determination and the rest were immediately gently shaken and used for the cataphoresis measurements.

It is doubtful, however, whether the soils had assumed their final charge. Since they had been kept dry for a considerable time it can be assumed that the gels were "aged" to an extent that they were acted upon too slowly by so dilute acid. Cataphoresis measurements should be made on moist soils, not on dried samples. Furthermore, cataphoresis is not always reliable for a determination of the isoelectric point because all inert substances charge themselves negatively in water. An ampholytoid which does not possess pronounced amphoteric properties may not develop a strong enough positive charge to become isoelectric at the chemically true isoelectric point.

For these reasons, and in order to save space, the entire results of the cataphoresis measurements will not be reported here. Only the isoelectric points thus determined (partly interpolated values) are reported (table 6). In the case of some of the A horizons no determination was possible, because of the formation of gas bubbles at the electrodes. In the case of profile 3 determinations were hardly possible in any horizon.

ELECTRODIALYSIS

The electrodialyses were made in the Mattson three-compartment cell, as thin a layer of soil as possible being used to shorten the time of electrodialysis

(4). The cell was placed in a 110 volt D.C. circuit in series with three 100-watt lamps placed in parallel. The water in the electrode chambers was changed at intervals of some hours, and when the experiment had proceeded so far that 2 or 3 hours' continued electrodialysis gave no reaction for bases with phenolphthalein the electrodialysis was considered complete. Generally it was so after 24 hours or a little more. In the case of the A horizons of the brown forest soils (profiles 1 and 3) a considerably longer time was required (45 and 48 hours). On the other hand the A_0 layer from the podzol profile 6 was very easily electrodialyzed though it contained fairly large amounts of bases. In fact, it was completely electrodialyzed after 4 hours, but in spite of that, the electrodialysis was continued for 24 hours as in the case of most of the other soils.

The amounts of bases made free by electrodialysis were determined by titration. An attempt was made to determine the diffusible anions also, but this was very often found to be extremely difficult because of humus coloration of the solutions. No exact values of the amounts of "adsorbed" anions can therefore be given. The amounts of electrodialyzable bases found are reported in table 6.

There is a very marked difference in the amounts and the occurrence of electrodialyzable bases in the brown forest soils and in the podzols. In the typical brown forest soil we find a fairly high amount of such bases in the mull, a much lower amount in the upper B horizon, and a continually decreasing amount in the deeper part of the profile. The aclimatic brown forest soil shows these same characteristics except that there is a much more marked maximum in the mull. To a certain extent the same distribution occurred in the podzols: the highest amount of bases is found in the humus layer, a much lower one in A_2, and generally a still lower one in B, but often an increase is again recorded in the deeper parts of B.

A comparison between the amounts of electrodialyzable bases found in brown forest soil and in podzol profiles from the same region and on the same parent material is of great interest. It was found, by comparing profiles 1 and 2 with 3 and 4, that the brown forest soils contain much higher amounts of bases. It is certain that this is one of the most important factors for maintaining the soil and vegetation types. On the other hand, the higher percentage of bases in the litter from a natural wood on brown forest soils tends to keep the soil in good condition, whereas a change in the vegetation, yielding a litter poorer in bases, can cause a degradation of the brown forest soil (2).

The high amounts of bases found in profile 5 as compared to the other iron podzols from the same place, profiles 4 and 6, can also be correlated with the good growth of the trees and the comparatively rich ground vegetation on the sample plot. In fact the vegetation type—the *Dryopteris*-type—where this profile was taken is the richest of all vegetation types on typical iron podzol in the region and, from the standpoint of the forester, one of the most productive.

ULTIMATE pH

Ultimate pH is the pH of the completely electrodialyzed material according to Mattson's definition (10). This pH depends upon the strength of the acidic and basic residues of the soil complex and is therefore closely related to the isoelectric point.

The ultimate pH was determined in the following very simple way. The completely electrodialyzed soil was shaken in a rubber-stoppered test tube with freshly boiled distilled water. The ratio of dry electrodialyzed soil to water was kept as narrow as possible (1:2). In the case of very humus-rich soils a wider ratio is necessary in order to get any liquid for the determination. Thus the ratio was 1:5 for the A horizon of profile 3 and 1:8 for A_0 of profile 6. After repeated shaking for a day the test tubes were left undisturbed for 2 or 3 days. After that time the supernatant liquids were clear enough to allow colorimetric pH determinations. These were made in the Hellige-Klett comparator with standard color discs and indicators. The indicators used were yellow, brom cresol green, brom cresol purple, and brom thymol blue. If a sample showed a pH within the range of two indicators it was determined with both, and the results were always the same. At the same time the actual pH values of the original, not electrodialyzed, soils were determined in exactly the same way. These were reported in the first part of this work but are quoted here again as a comparison with the ultimate pH. The results are seen in table 6.

The figures show that the ultimate pH is generally lower than the actual pH of the soil. This means that the soils are at least partly "saturated" with bases, which naturally must make the pH higher. Thus the bases present in the soil exert a certain resistance against the isoelectric weathering, and the freer the soils are from bases the more typical and responsive to the climatic conditions they are. The exceptions to the rule—some samples from profile 2—seem difficult to explain unless it be that this soil contains much soluble acids which go through the membrane during the electrodialysis.

The ultimate pH is lowest in the A horizon and generally increasing through the B and C horizons. This is true in most cases, but in two of the podzols (profiles 5 and 7) there is a maximum in the B horizon. There are only small differences in ultimate pH between the two soil types. The main difference is in the A horizon. The mull of the brown forest soils has an ultimate pH a little above 4. In the podzols, at least the upper of the corresponding layers, A_0 and A_2, is more acid, even as low as 3.5 in the case determined. The A_2 horizon has an ultimate pH about equal to that of the mull of the brown forest soils. A comparison between soils of the different types from localities near one another—profiles 1 and 2 and profiles 3 and 4—shows a slightly higher ultimate pH for the mull than for the podzol A_2 horizon, but the difference is so small that its significance seems uncertain.

Thus the ultimate pH gives a confirmation of the close relationship between

podzols and brown forest soils and at the same time shows a clear difference between them in the properties of the A horizon.

EXCHANGE NEUTRALITY AND COMBINING CAPACITY

When treated with a neutral salt solution, a completely unsaturated soil colloid, i.e., a colloid in which all diffusible anions and cations have been substituted by OH and H ions, for instance through electrodialysis, generally gives an exchange acidity. If the pH of the solution is adjusted by adding some free acid, a point can be reached where the colloid does not affect the reaction of the solution. This pH, according to Mattson's definition, is called "the point of exchange neutrality." The reason for the unchanged reaction is that at this point the displacement of OH ions by the anions of the salt just balances the displacement of H ions in the complex by the cations of the salt (10, p. 352). If more acid is added, the solution plus colloid will be less acid than the pure solution: the colloid gives an exchange alkalinity. Above the point of exchange neutrality the effect of the colloid is an exchange acidity, i.e., if alkali is added to the neutral salt solution the solution will have a lower pH in the presence of the colloid. In this way curves can be construed which give much valuable information about the properties of the colloid (13).

The form of the curves will depend on two things: the amount of the colloid present and its composition. The combining capacity for bases depends on the number of acid equivalents in the complex which are strong enough to be neutralized at the pH in question. This amount is naturally increased with increasing amounts of soil present, or, which is the same thing, with an increasing percentage of colloid in the material. Only one point will be the same: the point of exchange neutrality. This is, as seen from its definition, a qualitative property of the colloid and it is therefore constant within reasonable limits of concentration. This fact was proved experimentally by Mattson and Hester (13, p. 467).

From the curves we can immediately read the amount of base adsorbed at any pH above the point of exchange neutrality. At pH 7 we get, for instance, an exchange capacity comparable with the one determined in the common way. From the actual pH of the soil and the corresponding pH on the curve we can also obtain an estimate of the degree of saturation of the soil as well as its lime requirement. As pointed out by Mattson and Hester, the curves can be used for determining the amount of colloid present in the soil (13, p. 463).

Figures 6 to 12 show the results of determinations of exchange neutrality and combining capacity of samples from the different horizons of the seven profiles here previously described and discussed. The experiments were carried out exactly in the same way as described by Mattson and Hester, i.e., samples of the electrodialyzed soils were shaken in test tubes with N Na_2SO_4 solution containing different amounts of sodium hydroxide and sulfuric acid respectively. In each case 2 gm. of the electrodialyzed soil, calculated on the

oven-dry basis, was used, the volume of the solution being 10 cc. The small amount used for each determination is naturally a great source of error in the

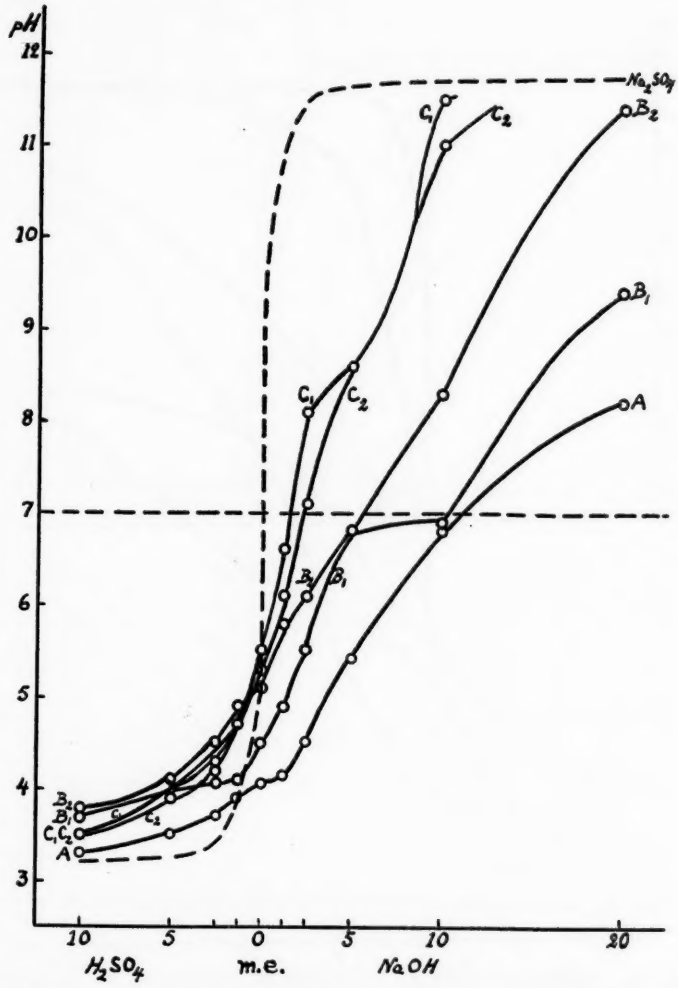

FIG. 6. THE pH OF EXCHANGE NEUTRALITY AND THE CAPACITY TO BIND ACID AND BASE OF ELECTRODIALYZED SAMPLES FROM THE DIFFERENT HORIZONS OF PROFILE 1 (TYPICAL BROWN FOREST SOIL)

case of these coarse soils. Larger amounts could not be taken, however, because of the comparatively small samples of the material at hand. After repeated shaking for some hours the test tubes were left undisturbed over-

night, and then colorimetric pH determinations of the clear solutions were made in the same way as described in the chapter on the ultimate pH. The indicators used were yellow, brom cresol green, brom cresol purple, brom

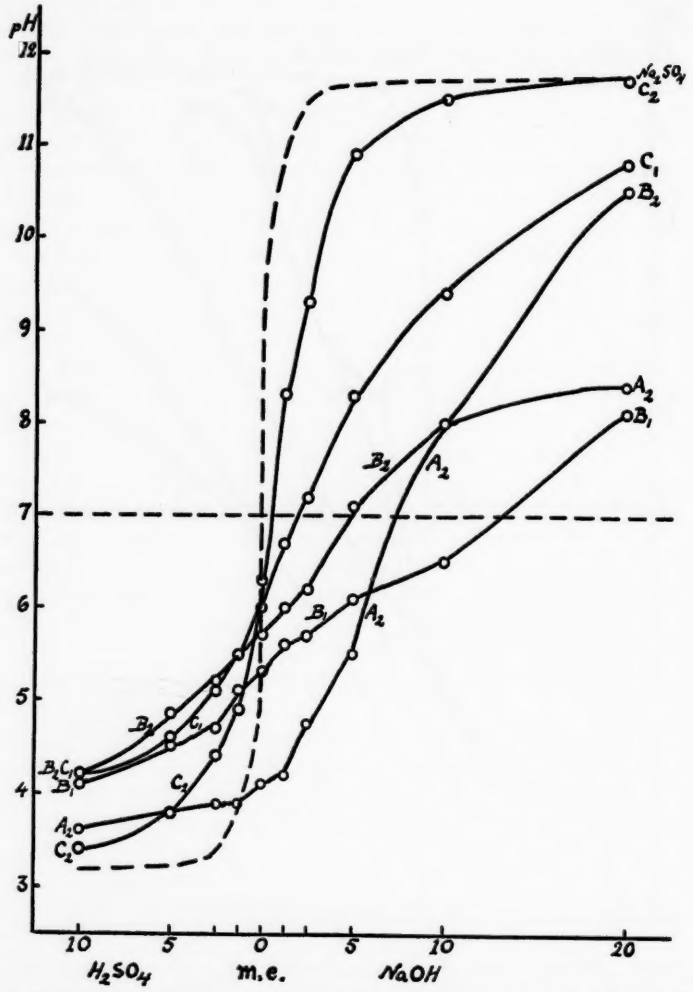

FIG. 7. THE pH OF EXCHANGE NEUTRALITY AND THE CAPACITY TO BIND ACID AND BASE OF ELECTRODIALYZED SAMPLES FROM THE DIFFERENT HORIZONS OF PROFILE 2 (PODZOL)

thymol blue, phenol red, thymol blue, thymol phthalein, alizarine yellow. Determinations were always made with two different indicators if the pH was in the range of both. The points of exchange neutrality, as read from the curves, are also to be found in table 6.

It is immediately seen that the tendency to variation in the pH of exchange neutrality is exactly the same as in the ultimate pH. There is always a low

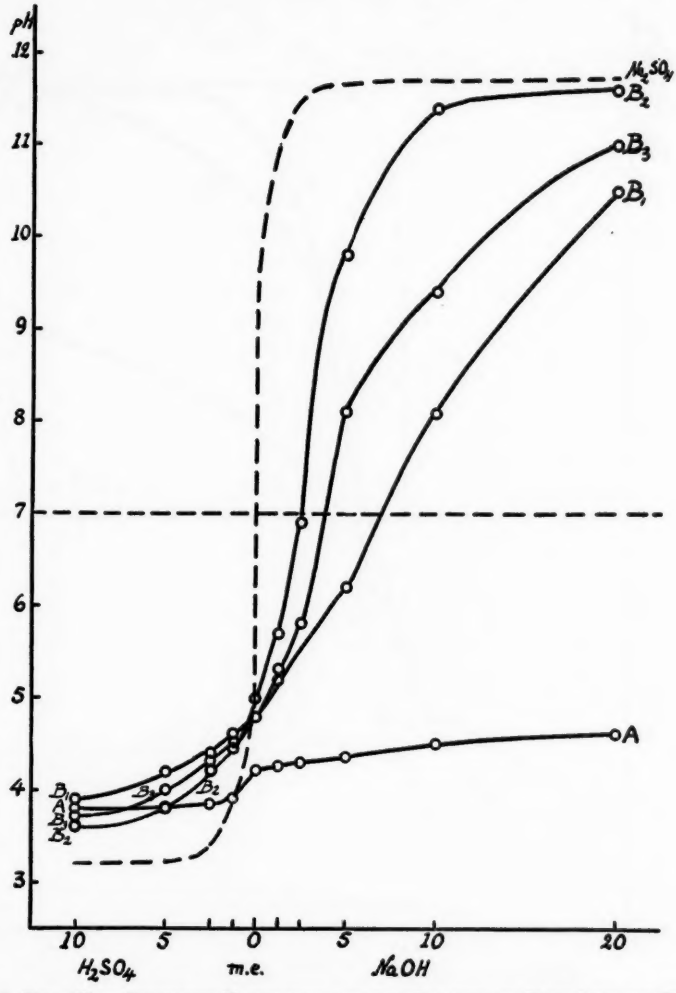

FIG. 8. THE pH OF EXCHANGE NEUTRALITY AND THE CAPACITY TO BIND ACID AND BASE OF ELECTRODIALYZED SAMPLES FROM THE DIFFERENT HORIZONS OF PROFILE 3 (ACLIMATIC BROWN FOREST SOIL)

pH of exchange neutrality in the A horizons. Generally it increases through the B horizons and is highest in C, in accordance with the theory. In the soils here investigated, the pH of exchange neutrality is often lower than the

ultimate pH. This is contrary to the results of Mattson and Hester (13, p. 462), but those results were obtained with soils very much richer in colloids.

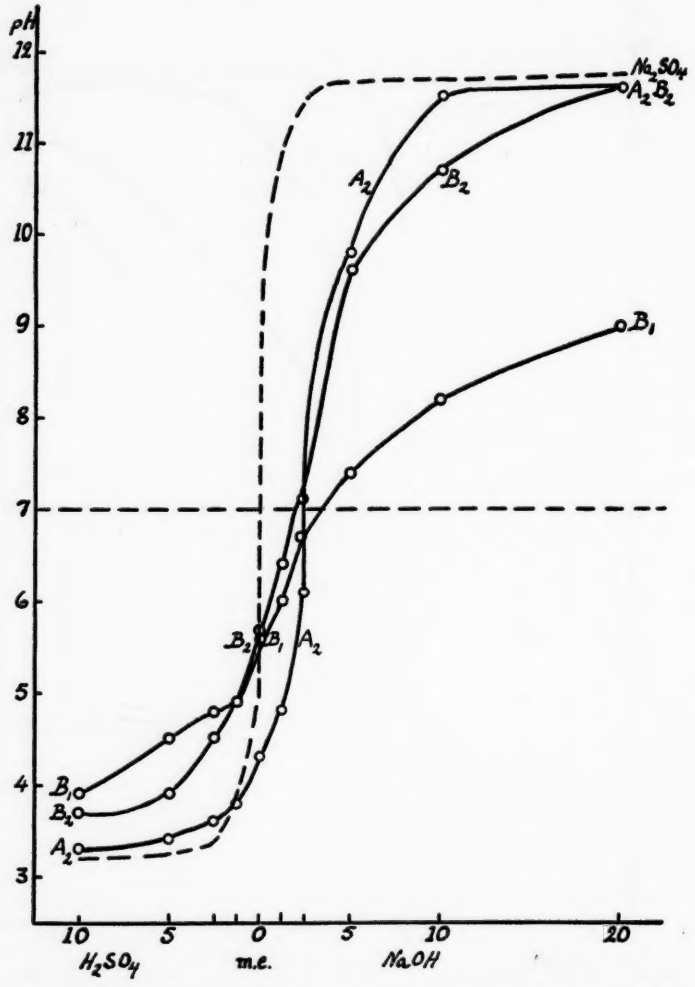

FIG. 9. THE pH OF EXCHANGE NEUTRALITY AND THE CAPACITY TO BIND ACID AND BASE OF ELECTRODIALYZED SAMPLES FROM THE DIFFERENT HORIZONS OF PROFILE 4 (IRON PODZOL)

It is therefore, easily explained: the dilution of the colloid when the ultimate pH is being determined is fairly high in the cases now reported and therefore the pH found must be somewhat higher than the real ultimate pH. There

are, however, several cases in the lower horizons where the pH of exchange neutrality is higher than the ultimate pH. This would indicate a high adsorp-

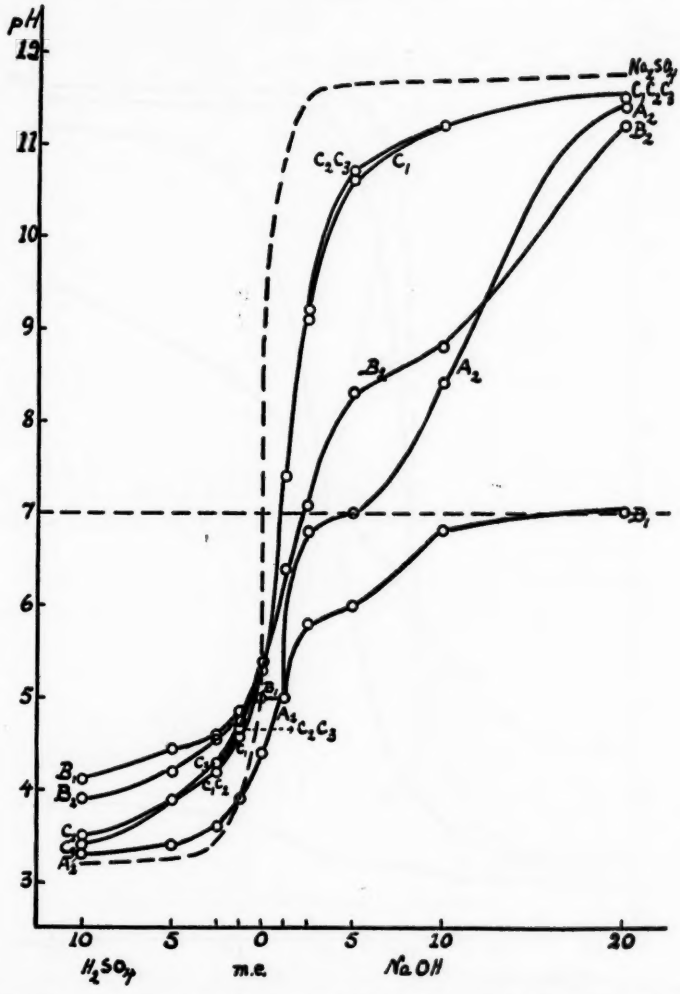

FIG. 10. THE pH OF EXCHANGE NEUTRALITY AND THE CAPACITY TO BIND ACID AND BASE OF ELECTRODIALYZED SAMPLES FROM THE DIFFERENT HORIZONS OF PROFILE 5 (IRON PODZOL)

tion of the SO_4 ion, which is pronounced when the sesquioxide content is high (13, p. 462). But the salt effect always makes the comparison uncertain.

The combining capacities for bases are also read on the curves. The

quantities depend, as previously stated, on the amounts of colloids present and on their composition. Any linear relationship between the combining

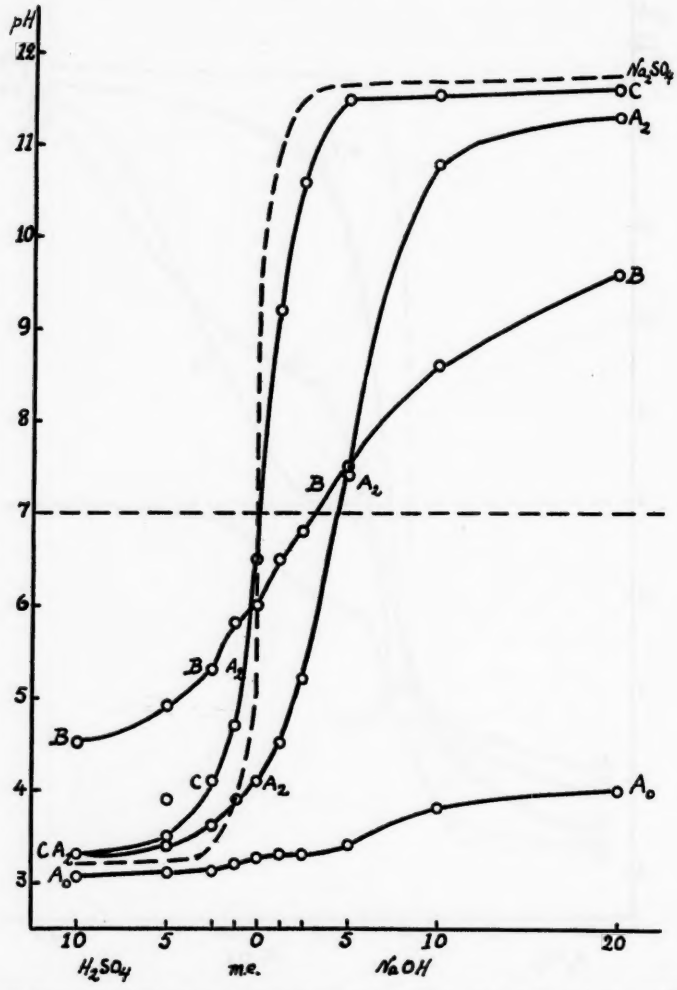

FIG. 11. THE pH OF EXCHANGE NEUTRALITY AND THE CAPACITY TO BIND ACID AND BASE OF ELECTRODIALYZED SAMPLES FROM THE DIFFERENT HORIZONS OF PROFILE 6 (IRON PODZOL)

capacities of the same soil at different pH values is not to be expected. It is entirely possible for a soil to have a very low combining capacity at a comparatively low pH, for instance at the point of neutrality, but this rapidly

increases with the pH because of continuous "liberation" of acid residues which are so weakly acidic that they cannot act as acids except at a high pH. Be-

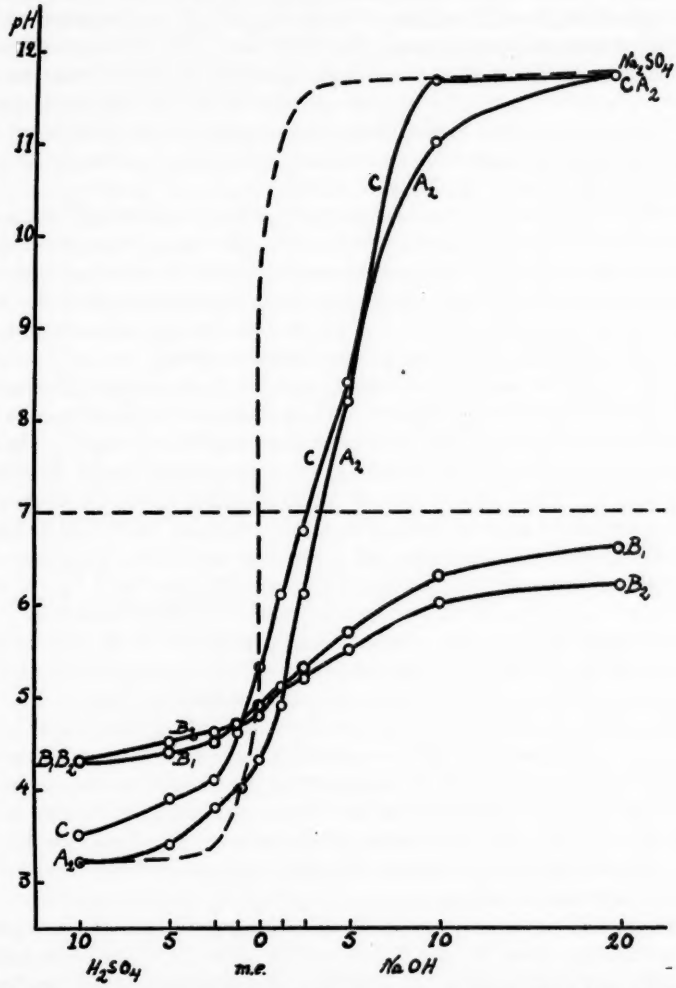

FIG. 12. THE pH OF EXCHANGE NEUTRALITY AND THE CAPACITY TO BIND ACID AND BASE OF ELECTRODIALYZED SAMPLES FROM THE DIFFERENT HORIZONS OF PROFILE 7 (IRON HUMUS PODZOL)

cause of the differences in the composition, the strength of the acid residues, and the different amounts of colloids present, the curves of combining capacity for different soil horizons have very characteristic shapes, as seen from figures

6 to 12. We find a maximum combining capacity in the A-horizon of the brown forest soils and the A_0 layer of the podzols. In the former, a more or less continuous decrease in combining capacity occurs with increasing depth throughout the B and C horizons, whereas the podzols are characterized by a minimum in A_2 and a maximum in the upper part of B. This shows that the amount of colloids is high in this horizon: qualitatively the exchange capacity must be higher in A than in B. The question of why the combining capacities at pH 7 determined by this method do not agree, except in a general way, with the base exchange values determined by leaching has already been answered by Mattson (13, p. 463).

In the case of brown forest soil the curve of the A horizon deviates widely from the curve of the Na_2SO_4 solution. At pH values below the point of exchange neutrality the distance between the curves is fairly small, showing that both the amounts and the strength of the basic residues are rather small. The curves intersect at a fairly low pH, and on the right side of this point, the point of exchange neutrality, the distance between the curves rapidly increases. This means that the colloid complex has a strong acid residue as well as a strong neutralizing power. The latter must be due either to a high colloidal content or to a low acid equivalent weight or to both. The acid equivalent weight of humus is usually much lower than that of the mineral soil colloids. The position of the B curves indicates a different composition of the colloid. Below the point of exchange neutrality the curves lie higher, which, together with the higher pH of exchange neutrality, must mean that the basic residues are stronger than in A. On the other hand the B curves are closer to the Na_2SO_4 curve above the point of exchange neutrality. The organic part of the colloid complex is higher in A than in B, and therefore the qualitative differences in the colloids govern the form of the curves. The form of the C curves shows a lower amount of colloids in C than in B.

The curves for the aclimatic brown forest soil (fig. 8) are of very nearly the same type, except that the curve of the A horizon is still more "flattened." It does not intersect with the line representing pH 7 before a point corresponding to a combining capacity of about 60 m.e. of NaOH per 100 gm. of soil. The point is very uncertain because of the strongly colored solution obtained after the salt solutions are added. This coloration is due to humus and shows a high dispersion or solution.

The podzol curves are very different. The general form of the A_0 curve is to a certain extent like the A curve of the aclimatic brown forest soil (see fig. 11), but there is still a big difference. No intersection with the Na_2SO_4 curve was found; the A_0 curve ran below the Na_2SO_4 curve all the way on the acid side. This would indicate that no basic residues are present, that the colloid complex is not amphoteric, and hence that no point of exchange neutrality exists. From the theoretical standpoint it must be expected that the curves intersect farther out on the acid side, at least they should run together asymptotically. The gradual slope of the curve shows that the intersection

with the pH 7 line lies far above a concentration of 20 m.e. of NaOH per 100 gm. soil. The A_2 curves (see fig. 9–11) approach the Na_2SO_4 curve fairly closely on both sides of the point of exchange neutrality; this is true also for the C curves, whereas the B curves are less steep. The composition of the colloids in A_2 compared to those in B would naturally give less steep A_2 curves. But now the quantities of colloids present in A_2 are very low compared to those in B, as indicated by the oxalate analyses (3, p. 149). Therefore, the qualitative difference is not seen except on the acid side of the point of exchange neutrality. Here the B curves run above the A_2 curves, just as their higher relative content of basic residues requires. But even here the higher content of colloids has its natural influence. The podzol curves are of very much the same type as those obtained by Mattson and Hester from the Lakewood podzol (13, p. 471). The differences in the C curves are certainly due to the higher maturity of this soil: the soil-forming processes are evident even in the deepest part of the profile.

Figure 12, for profile 7, shows the very high amounts of colloids in the B horizons of a profile of the iron humus podzol type. There are high amounts of both acid and basic residues in the colloid complexes as seen from the gradual sloping of the curves on both sides of the fairly high point of exchange neutrality. These facts agree very well with the results of the oxalate analyses previously reported (3, p. 149, 152–153).

Table 6 also gives a comparison between the percentage base saturation in the different horizons of the soils. The figures are calculated from the values read on the curves (fig. 6 to 12) and represent the relation $\frac{a}{b} \cdot 100$, where a is the amount of base combined at the actual pH of the soil and b the base combined at pH 7. In A of the typical brown forest soil and of the aclimatic brown forest soil we find a high base saturation. The true iron podzols have a very low, or even negative, base saturation in A_2. The results show a clear difference between podzols and brown forest soils. In respect to base saturation the iron humus podzol seems to take a middle position between podzols and brown forest soils. An interesting case is podzol 2 where all the values are negative. This must mean that all the horizons here are to a certain extent saturated with acids. The same conclusion was previously drawn from the determinations of the ultimate pH.

It is seen that the determinations of the point of exchange neutrality and of the combining capacity of the different soil horizons give very good information about the differences between the two soil types brown forest soils and podzols. The former gives the strength of the acid and basic residues, whereas the latter gives the capacity of the soil to bind acids and bases. Furthermore, the method gives an easy way of determining the degree of base or acid saturation. The results show that the podzols develop through weathering an upper strongly acidoid mineral horizon whereas the brown forest soil profile shows strong acidoid character in the uppermost humus horizon only.

After this paper was written new investigations were published by Mattson and Gustafsson concerning the properties of some Swedish podzols (12). Working with methods similar to those used here they obtained comparable results. There are some differences, however. According to Mattson and Gustafsson the actual pH of the soil solutions in the B and C horizons of podzol profiles is lower than the ultimate pH of their colloidal complexes. As seen from table 6 this is not always the case in the soils here investigated. The following explanation is suggested for this. The actual pH of the soil solution varies somewhat, depending on several circumstances. The soil solution may for some time have a higher or lower pH than the one corresponding to equilibrium conditions with the colloid. The ultimate pH should be a fairly constant quality in each soil horizon, showing the net result of the prevailing weathering. Equilibrium conditions cannot be expected to occur simultaneously with a more or less occasional pH.

SUMMARY

The podzol and brown forest soil profiles described in the first part of this paper are further investigated with methods aiming at determination of the amphoteric properties of the soil colloids.

It is shown that base exchange, cataphoresis, ultimate pH, exchange neutrality, and combining capacity give reliable information about the soil forming processes and more or less accurate distinctions between the soil types investigated. Theoretical discussions show that the methods can also be applied for the same purpose in the case of other soil types.

The theory of Mattson of isoelectric weathering is confirmed. The results show that all the soils tested have developed through an acid type of weathering, the podzols being the result of a most acid weathering, the typical brown forest soil originating from a less pronounced acid weathering, and the "aclimatic" brown forest soil taking a middle position between those two soil types, just as could be expected from their occurrence in nature.

Methods such as determinations of the ultimate pH, the pH of exchange neutrality, and the combining capacity at different pH will permit a rapid and conclusive comparative study of the soil forming processes in different soil regions.

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